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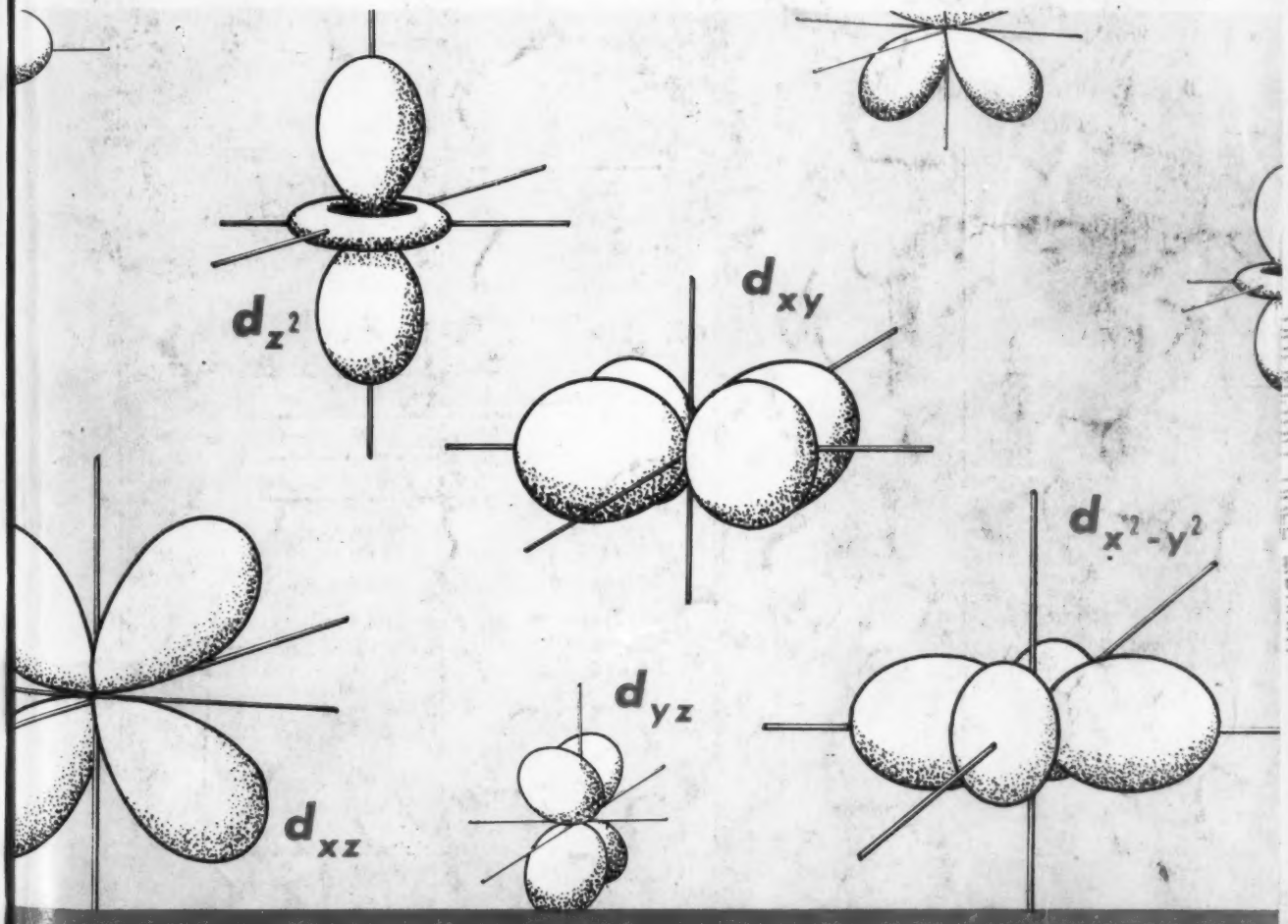

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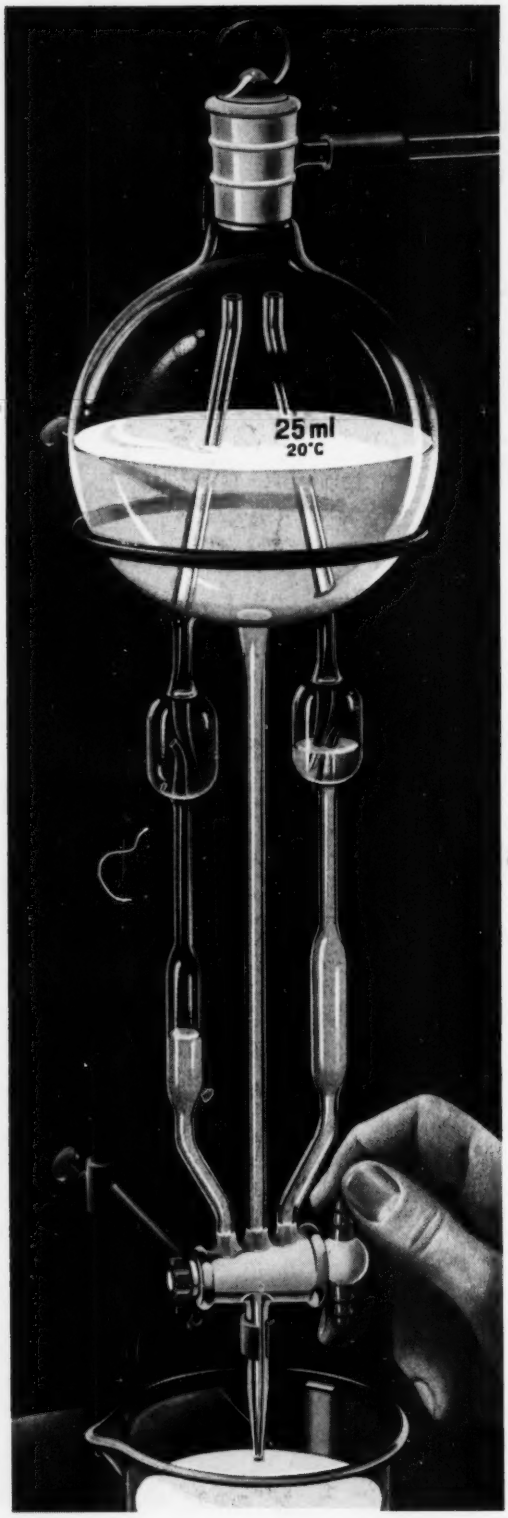

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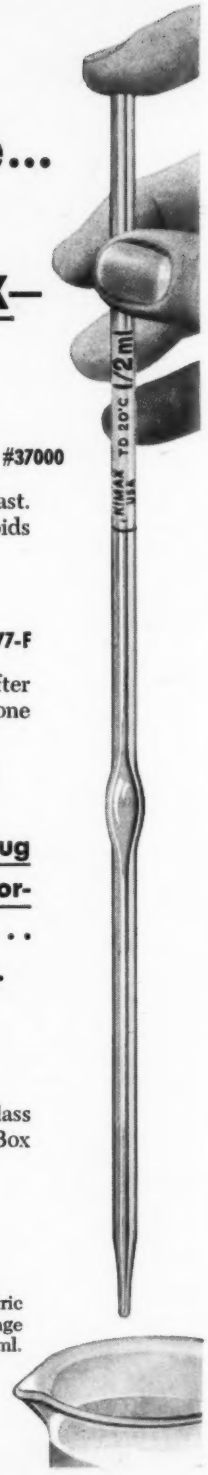

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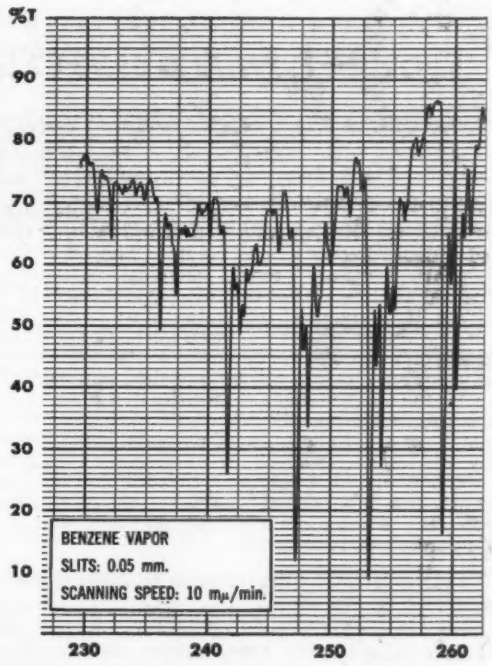

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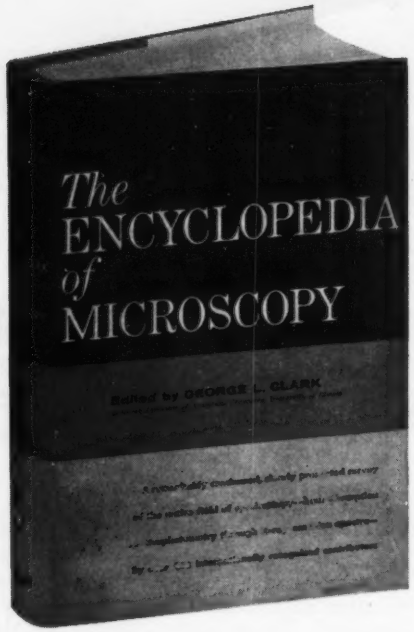

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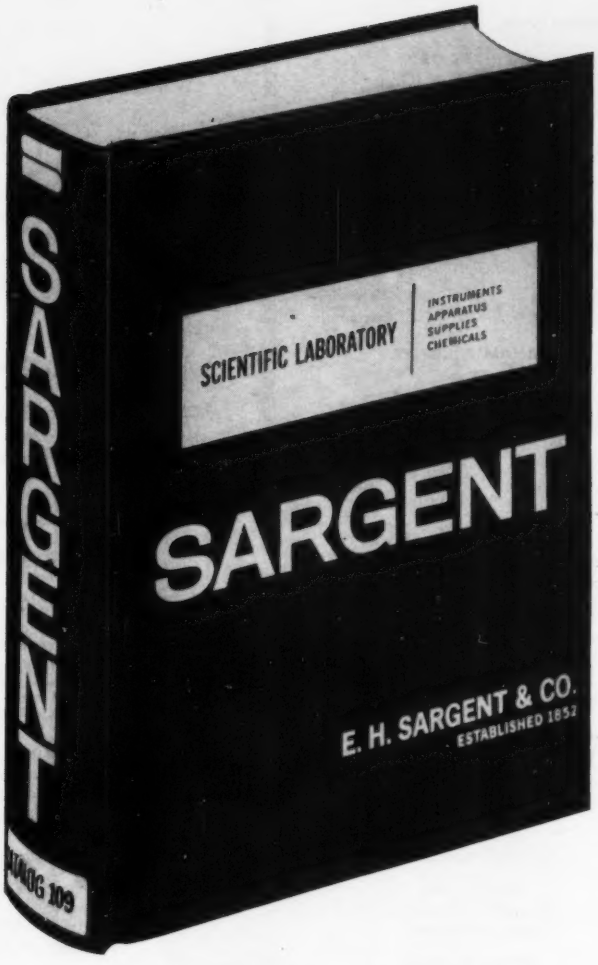

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13. Nuclear Radiation Electronic Gear

The signals from nuclear radiation detectors are generally of low magnitude, brief duration, and high frequency. In order to read out these signals in a useful way, it is necessary to use rather sophisticated and elaborate electronic gear in conjunction with the detector. The characteristics of the electronic equipment are, of course, determined by the nature of the detector and the use to be made of the read-out signal.

The fundamental types of electronic circuitry needed with nuclear radiation detectors are (*a*) *power supplies*, (*b*) *amplifiers*, and (*c*) *scalers*. A power supply is needed to provide the accelerating voltage for the detector, as well as the operating and reference voltages for vacuum tubes and transistors in the circuitry. If the detector is a Geiger-Mueller counter operated on the plateau of its voltage-characteristic curve, an *unregulated* power supply may be employed. In this type of power supply no special components or circuitry are added to maintain the output voltage constant despite variations in the line voltage, ambient conditions, tube characteristics, etc. When the greatest reproducibility is desired in G-M counting, and for practically all measurements with proportional and scintillation counters, a *regulated* power supply is employed. The design of these devices includes provision for buffering the output voltage against moderate variations in operating conditions.

An amplifier is required to magnify the primary signal from the detector to the point where it can be handled by the read-out device. The first stage of amplification is often called the *preamplifier*, and may be physically separated from the rest of the amplifier. Thus, the preamplifier is often incorporated in the base of the tube socket of the G-M tube, photomultiplier, etc., and its output is fed by a cable into the amplifier proper. The close proximity between detector and preamplifier serves to minimize the pick-up of stray signals radiated from other equipment, which at this stage in the amplification might seriously distort, or mask entirely, the low-level detector signal. A great variety of amplifiers is in current use; these include linear amplifiers, fast pulse amplifiers, non-overloading amplifiers, amplifiers with pulse height discrimination, coincidence or anti-coincidence amplifiers, and others.

The scaling circuitry is employed to scale down the rate at which pulses are delivered from the amplifier, so that a mechanical register can record the pulsing rate without excessive losses due to the dead time and inertia of the mechanical movement. Thus, a scaler is essentially a frequency divider, and the division factor is the *scale* of the instrument; e.g., a "scale-of-64" circuit gives output pulses at $^1/_{64}$th of the rate of the input pulses fed into it.

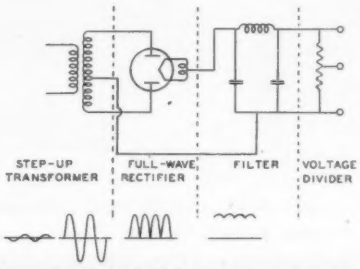

Figure 1. A simple high voltage power supply.

The output pulses from a scaler may be fed into a *mechanical register*, which records in digital form the total number of pulses received; or the scaler output may be fed to a *ratemeter* circuit, which partially integrates the charge involved and presents this information in the form of a deflection of a D'Arsonval meter indicator. The ratemeter may be calibrated to be direct-reading in terms of counts per unit time. When a mechanical register is used to totalize the number of output pulses from a scaler, a high precision *timer* must be employed, so that the number of pulses detected per unit time can be calculated. In most scalers, the scaling stages have visual indicators that show the number of pulses which have passed through the circuit, and in some instruments the total count is read from these indicators directly.

Power Supplies

Most nuclear radiation detectors require moderate to high voltages for their operation; these voltages range from 100 v to over 2500 v. It is now almost universal practice to obtain such voltages from either a small number of radio-type batteries (for portable, survey instruments), or from the electric utility power line (usually 110 v, 60 cycles per sec in the U. S.). In either case, it is generally necessary to step up the input voltage to the desired output level.

If the supply voltage is ac, it is stepped up by means of a high voltage transformer, then rectified and filtered, as shown in Figure 1. If the supply voltage is dc, it is necessary first to convert this into ac, and then to step up the ac, rectify it, etc. The conversion of dc to ac may be done mechanically or electronically.

Figure 2 shows a diagram of a simple survey meter in which the high voltage is obtained by manually pressing and releasing a pushbutton switch a number of times. When the push switch is depressed and contact is made, current starts to flow, and builds up to its Ohm's law magnitude at a certain rate. This transient current change is equivalent to an ac signal, and a voltage is induced in the secondary winding of the transformer. However, when the pushbutton is released, the breaking

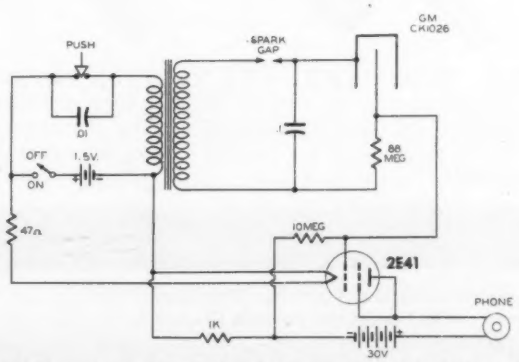

Figure 2. The Detectron Co. Model DG-5 Portable Survey Meter, in which the high voltage for the G-M tube is obtained as a result of operating a pushbutton switch in the primary circuit of a step-up transformer.

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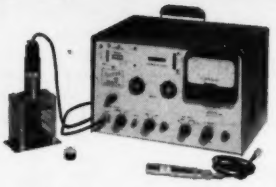

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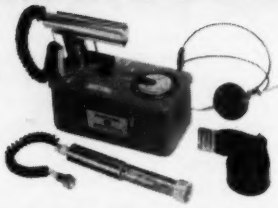

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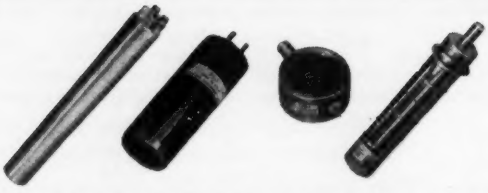

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of the circuit is more abrupt than was the make, and the new transient drops more rapidly. This is equivalent to a larger ac signal, and a larger voltage is induced in the secondary winding. The spark gap is adjusted so that it fires and passes only the larger voltage pulses. When the spark occurs, charging current flows into the 0.1 mfd condenser, and the voltage across this component builds up to about 900 v. As the stored voltage is dissipated, it can be restored simply by operating the pushbutton a few times. The pulses from the G-M tube are amplified by the 2E41, and the variations thereby generated in the plate current of this tube produce audible clicks in a magnetic headphone.

Some commercial portable survey meters based on this principle employ a buzzer-type electromagnetic vibrator to chop the dc into ac (e.g., Nuclear-Chicago's Super-sniffer; Anton Electronic Lab's Radiac Set).

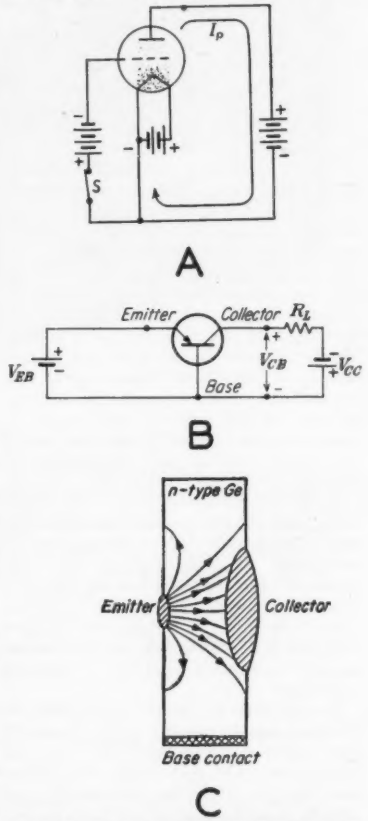

Figure 3. Illustrating the equivalence in application of a triode vacuum tube and a transistor. A. In the triode circuit, the cathode-to-plate current is modulated by the grid voltage. B. In the transistor circuit, the flow of holes from the emitter to the collector is modulated by the base current. C. Flow pattern of holes from emitter to collector in n-type semiconductor.

The electronic approach to conversion of dc to ac makes use of the ability of a vacuum tube or transistor to function as an oscillator if the capacitance and inductance in its plate and grid, or collector and base, circuits have the right values.

(*Continued on page A229*)

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The equivalence between a triode vacuum tube, and a point contact transistor is illustrated in Figure 3. In both cases, the flow of electrons from the negative electrode to the positive electrode is modulated (helped or hindered) by the charge on the third, control element (grid or base, respectively). If the plate (or, emitter) and grid (or base) circuits are suitably coupled together, e.g., through a capacitance or inductance, an increase in the electron current flowing to the plate or emitter can induce a positive-going effect on the grid (or, base), which has the effect of causing the tube or transistor current to increase still more, which produces a further positive-going effect on the control element, etc., etc. This *regenerative process* causes the current to increase to the maximum value that can pass under the given circuit conditions. When this maximum is reached and the current increase ceases, the positive-going effect on the control electrode begins to dissipate, which is equivalent to the onset of a negative-going effect from the previous positive maximum. This causes the current to begin to decrease, which in turn induces a larger negative-going effect on the control electrode, which reduces the current still further, etc., etc. Thus the current oscillates continually between a maximum and a minimum value. It will be noted that the supply voltage applied across the vacuum tube or transistor is not alternating, but is direct. The alternation in current magnitude is due entirely to the nature of the coupling between plate (emitter) and grid (base) circuits, and not to the supply voltage. Transistors are low-voltage circuit elements, and function on supply voltages as low as tenths of a volt; vacuum tubes generally require tens to hundreds of volts for satisfactory operation. Figure 4 shows the circuit diagram of the Sparrow survey meter ($79) of Gelman Instrument Co., Chelsea, Michigan, which employs a transistor oscillator to step up the voltage from two $1^1/_2$-v penlight batteries to the level of 500 v needed to operate the G-M counter tube.

For survey, health monitoring, or prospecting work, simple unregulated power supplies such as those described above are quite adequate. However, for quantitative measurements it is usually desired to regulate the output voltage of the power supply. This is commonly done by the use of (*a*) voltage regulator tubes, or (*b*) electronic regulating circuits.

Regulated Power Supplies

A voltage regulator tube is simply a two-electrode tube containing a gas that will support a glow discharge between the electrodes. A minimum, or firing voltage that is larger than the operating voltage must be applied to cause the discharge to form in the tube, but once initiated the discharge itself tends to maintain a constant voltage difference between the electrodes, if the circuit permits this to happen. Figure 5 illustrates the type of circuit that must be used. When a discharge exists, the gas between the elec-

(*Continued on page A230*)

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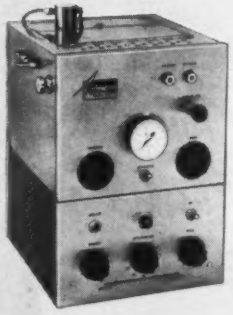

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trodes is partially ionized, and electrons flow from the negative electrode to the positive one through a space charge of the relatively much slower moving positive ions. The voltage drop across the tube is equal to the discharge current times the resistance of the gas plasma ($V = I \times R_{gas}$). If the supply voltage were to increase, this would cause the current through the entire circuit to increase; the enhanced flow of electrons through the tube would correspond to increased ionization of the gas and hence to an increased positive ion space charge. This greater ionization increases the gas conductivity, i.e., decreases the tube resistance, so that although I has gone up, R_{gas} has gone down, and V ($= I \times R_{gas}$) can remain substantially constant. Thus, the entire increase in the supply voltage, E_{in}, appears as an increased IR-drop across the resistor, R, and the voltage across the tube, E_{out}, is not affected. Voltage regulator, or VR-tubes are available which are capable of maintaining fairly constant voltages at various values in the range from 30 to 150 v, depending upon electrode spacing, area, and gas filling. (Tubes employing a high-voltage corona discharge are available for regulating voltages up to 700 v and higher, but the constancy is not as good as the glow tubes provide). A string of six or more VR-tubes in series can be used to give a total regulated voltage that is large enough to be suitable for radiation counter tubes. An example of a commercial power supply of such a type is the Model 312 High Voltage Power Supply ($465) of Baird-Atomic, Inc., Cambridge, Massachusetts, shown in simplified diagram in Figure 6.

(*Continued on page A234*)

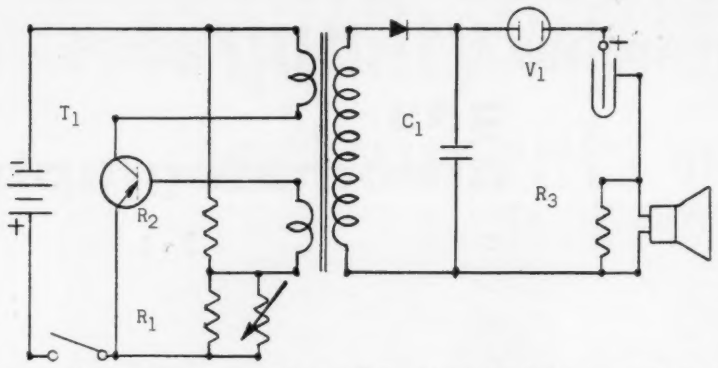

Figure 4. Schematic of the Sparrow miniature radiation detector of Gelman Instrument Co., in which the high voltage is obtained from the stepped-up output of a transistor oscillator.

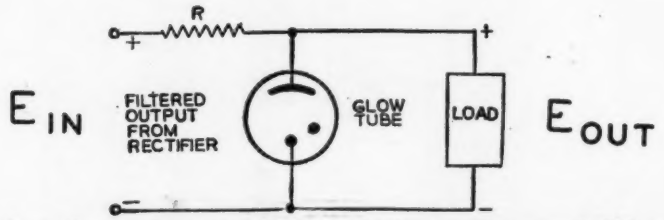

Figure 5. A voltage regulator tube maintains a regulated output voltage across itself, E_{out}, despite variations in the applied voltage, E_{in}. The resistor, R, is necessary, for all the voltage variations appear across it.

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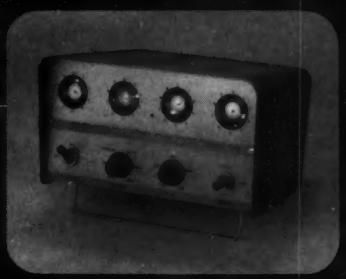

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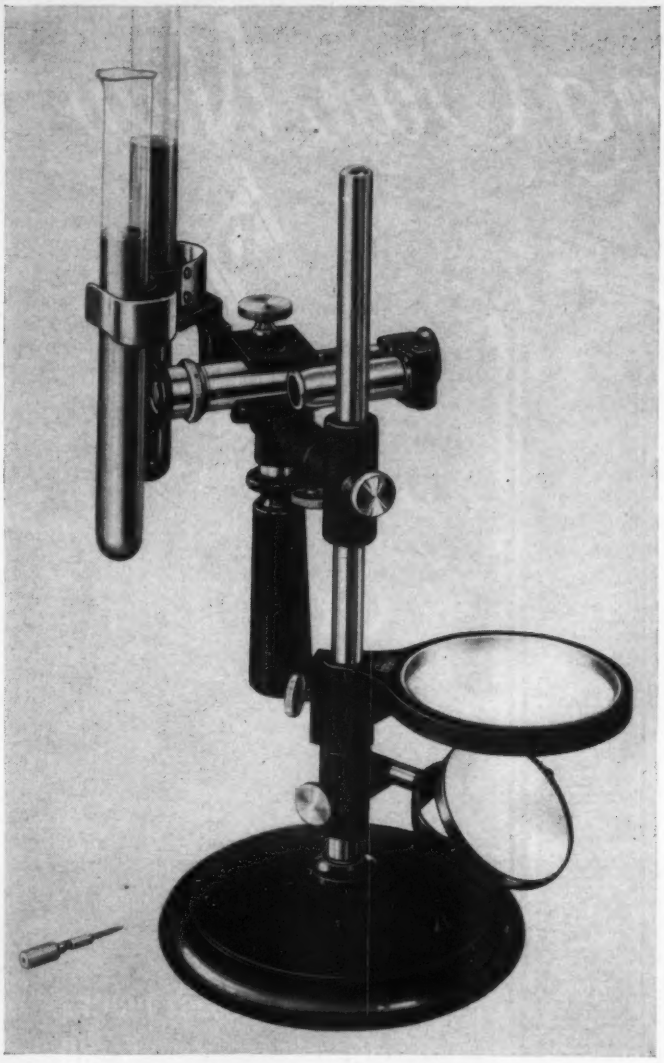

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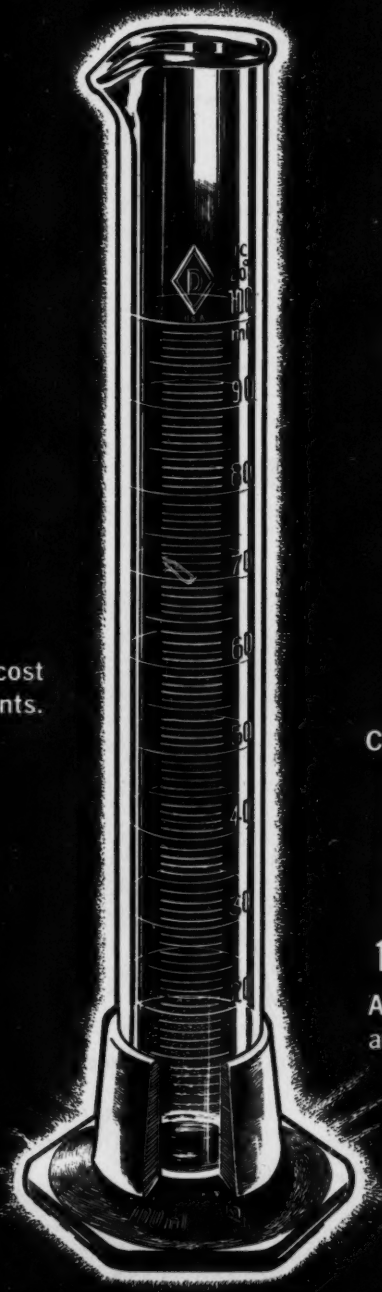

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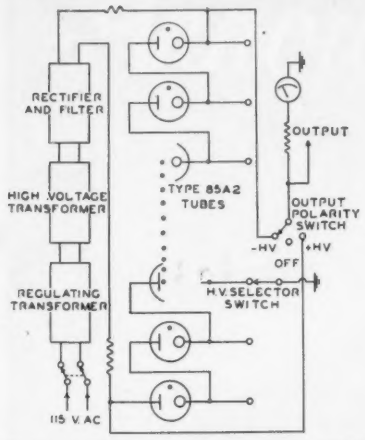

Figure 6. Schematic of the power supply design of the Baird-Atomic Model 312 High Voltage Power Supply.

The control principle of one type of electronically regulated power supply is illustrated in Figure 7. A triode vacuum tube is placed in series with the load, so that the output voltage from the power supply filter section is applied across the pair. The potential of the grid of the vacuum tube, E_2, is established independently of the rest of the power supply by a separate battery and slidewire. The grid potential, E_2, is adjusted relative to the voltage across the load, E_1, until the tube passes the desired current. If the output voltage were to increase, the potential of the tube cathode would tend to become more positive. This would make the grid appear to become *more negative*, since it is only the *relative difference* of potential between grid and cathode that is important, and the potential of the grid is held constant by its battery. Hence, the increased output potential causes the vacuum tube to show a greater resistance to the passage of current, leaving the current (and voltage) across the load substantially constant. The increased voltage all appears across the tube, due to the increased tube resistance ($V_{tube} = I \times R_{tube}$). The electronically regulated power supplies used in nuclear detection work are often considerably more sophisticated in design than the simple circuit just described, although the basic principle still applies. An example of a regulated power supply with a constancy of output of $\pm 0.005\%$ at voltages up to 2500 v is the Model HVS25-CT ($795) of Victoreen Instrument Co., Cleveland 3, Ohio, illustrated in block diagram in Figure 8. In this instrument, the output voltage is compared with a stable reference voltage, and the difference signal is employed to correct the output as may be necessary in order to maintain it at any preselected level.

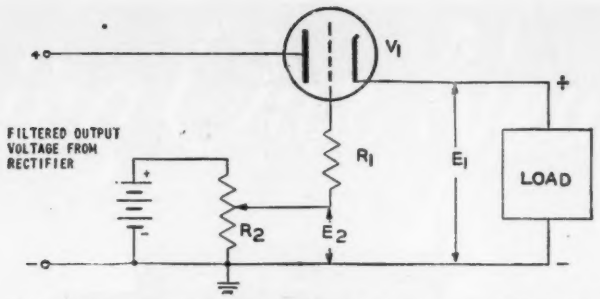

Figure 7. Simple electronic regulator circuit, in which the triode acts as a variable resistance, increasing when the supply voltage increases, and decreasing when it decreases. This effect is achieved by maintaining an independent and constant grid voltage.

Amplifiers

The requirements that must be satisfied by the amplifier differ with the radia-

(*Continued on page A238*)

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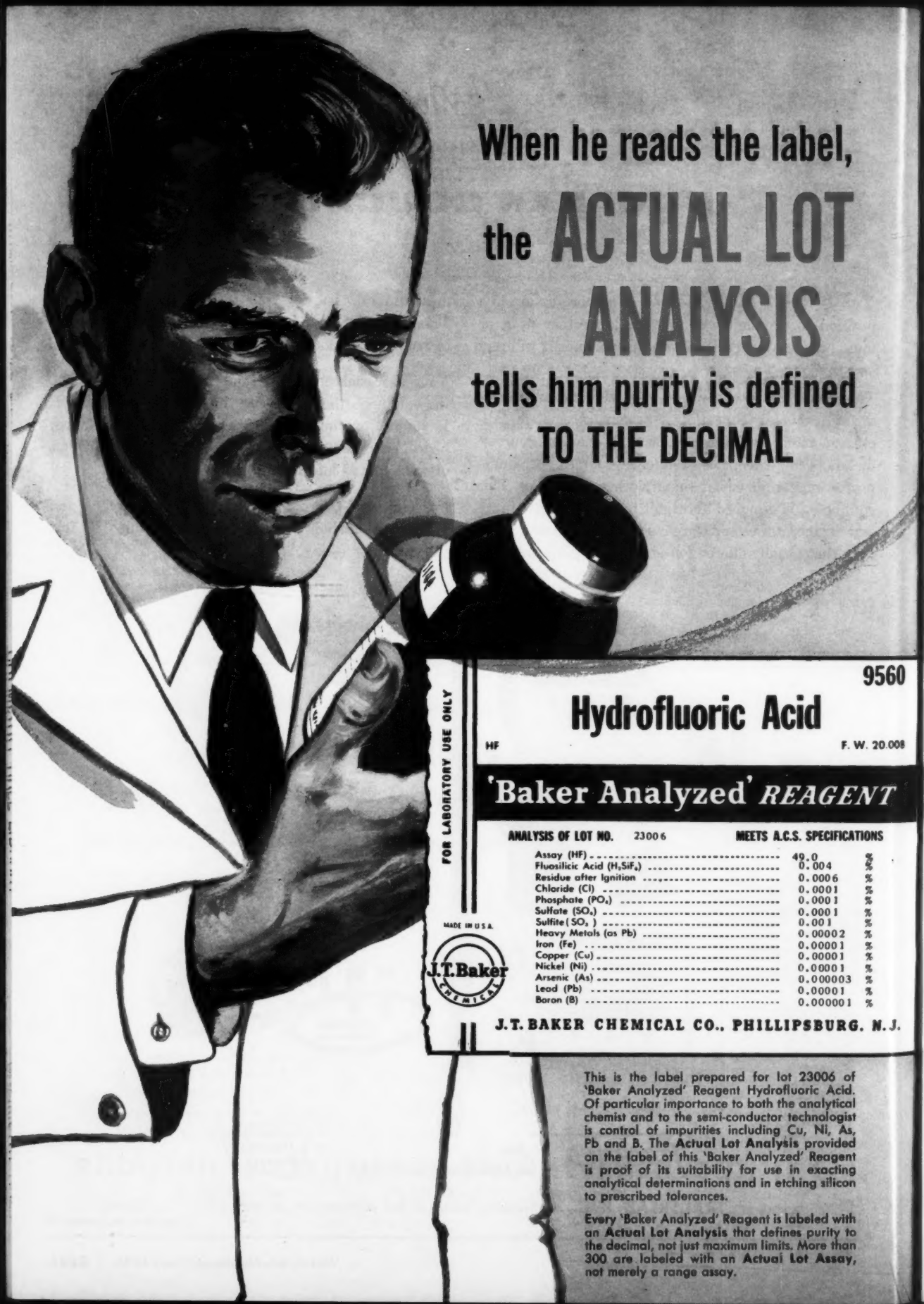

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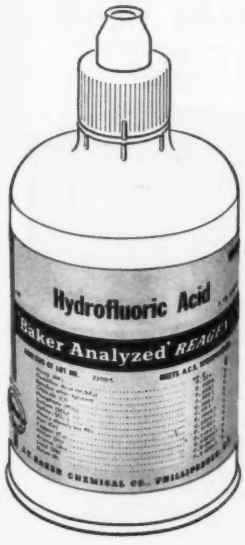

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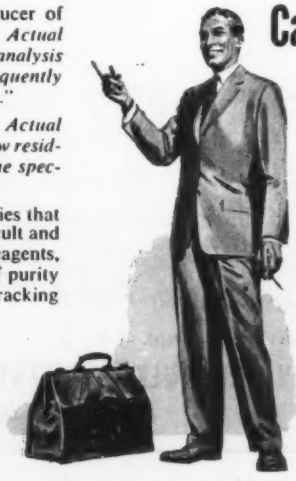

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tion detector and the type of information sought. With ion chambers, the amplifier must have an exceedingly high input resistance (very low grid current, very high insulation resistance between the grid and the other tube elements), and should be capable of giving a reliable read-out for currents as low as 10^{-15} amp. With pulse-counting tubes, there is the additional requirement that the amplifier must be fast in response and recovery.

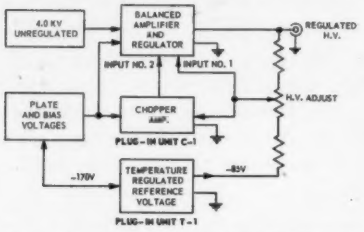

Figure 8. Block diagram of the design of the electronic regulating circuitry employed in the Victoreen Model HVS–CT series of power supplies.

With proportional counters and scintillation spectrometers, the amplification of the pulses must be linear over a considerable range of pulse sizes.

The same type of electrometer amplifier that was treated in detail in the earlier discussion of pH meters is useful in ion chamber measurements. The FP-54 electrometer tube has been widely used for this purpose, and a typical circuit is shown in Figure 9. This is sometimes called the DuBridge-Brown circuit; the cathode-to-plate voltage is only about 5 v, and the plate current is read on a sensitive galvanometer. The signal from the ion chamber flows through the 10^7 — 10^{11} ohm grid resistor, generating an IR-drop that is impressed between grid and cathode and controls the plate current. Ion chamber currents of 10^{-14} amp can be reliably measured with this circuit. A series of electrometers of this general design, based upon the 5889 electrometer tube, is commercially available from Victoreen Instrument Co. Their linear electrometer is available with nine ranges, from 10^{-3} to 10^{-11} amp full scale, and one model (Model VTE-1, $395) provides a bucking current of either polarity variable from 10^{-3} to 10^{-9} amp, to permit enhanced sensitivity in the measurement of small current variations above a large, steady background current. Model VTE-2 ($395) provides thirty linear ranges from 1×10^{-3} to 2×10^{-13} amp. A logarithmic read-out instrument, in which the range from 10^{-4} to 10^{-12} amp is covered by a single full-scale meter deflection, is available for measurements where rapid, large variations in ion chamber currents are observed, as in nuclear pile work. The logarithmic function is generated by applying the output signal of the standard electrometer amplifier to a diode tube which is biased so that its voltage-current characteristic is logarithmic.

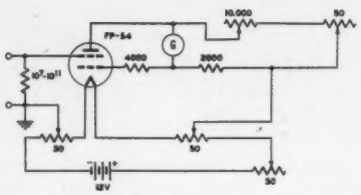

Figure 9. Schematic of a simple, low-voltage electrometer circuit for amplification of ion chamber currents.

A more sensitive and rugged amplifier for very small ion chamber currents can be constructed on the basis of the vibrating (dynamic) condenser input principle. Figure 10 shows a schematic of the design of the Cary line of electrometers (Model 32, $1100). The input signal, introduced at *I* in the diagram, may either directly charge the fixed plate of the condenser, C_v, or by flowing through a calibrated high resistance placed at R_i generate an IR-drop that establishes the charge on the condenser. An oscillator vibrates the moving plate ("reed") of the condenser at 450 cps, causing the capacitance to vary with this frequency, and producing an ac voltage across C_v which is proportional to the impressed dc signal from the ion chamber. This ac voltage is amplified in the ac amplifier, then rectified in the synchronous rectifier. The rectifier output, which is proportional to the input dc voltage, is filtered and causes current to flow through the feedback resistors and through the meter circuit. The amplification is stabilized by the feedback,

(*Continued on page A241*)

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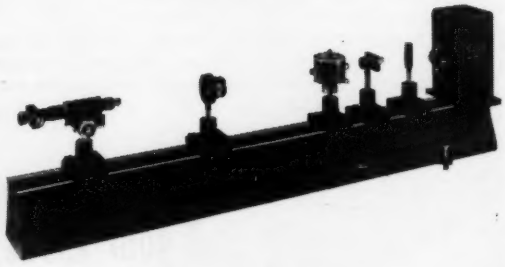

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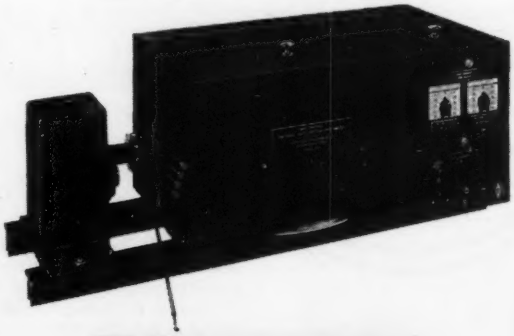

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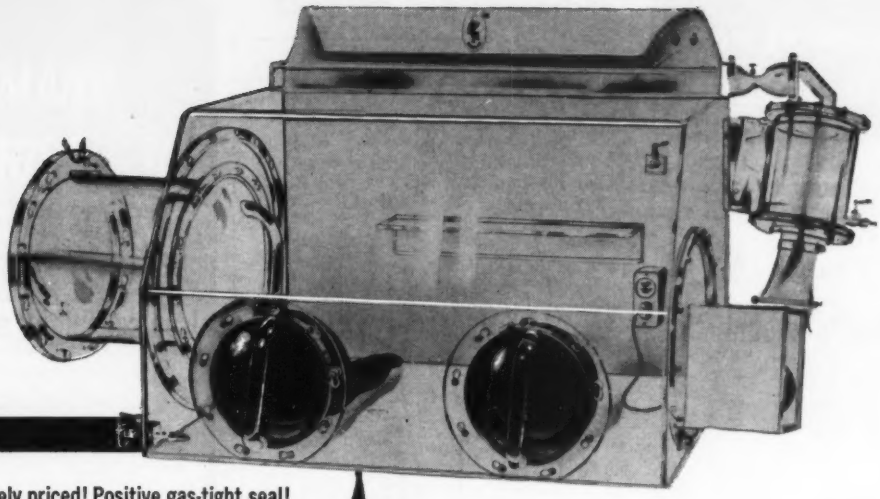

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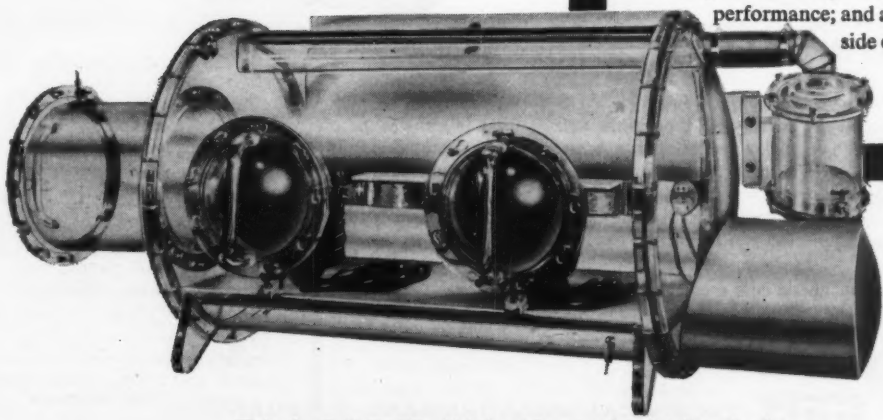

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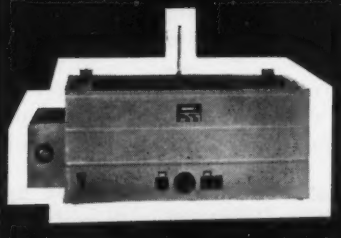

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and the feedback current is itself the output signal. This electrometer has a short period noise level of less than 6×10^{-16} coulombs rms on open circuit, or 0.02 mv rms on closed circuit, and the steady drift is less than 5×10^{-17} amp on open circuit, or 0.1 mv per day on closed circuit.

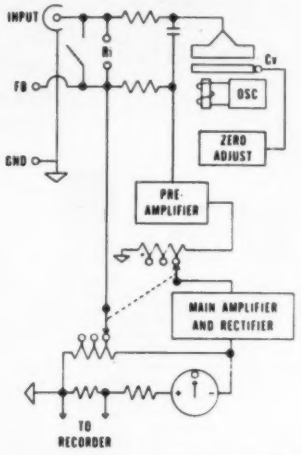

Figure 10. Block diagram of the amplifier design employed in the Cary line of vibrating condenser electrometers. C_v is the condenser, consisting of a fixed plate and a vibrating reed. R_i is for the addition of a calibrated high value resistor, for the measurement of currents and voltages in the higher ranges. *FB* is feedback terminal.

The Model 32 can be employed with a suitable ion chamber to detect as little as 5×10^{-15} curies of C-14 per mg of $BaCO_3$, or 10^{-10} curies of H-3 per mg of hydrogen. The Model 31 electrometer ($1650) consists of two parts; an electrometer head is connected by cable to the main amplifier. It is adaptable to a wide range of measurements of small currents, charges, or voltages.

The Model 6000 Dynacon Electrometer ($1775) of Nuclear-Chicago is similar in design to that just described.

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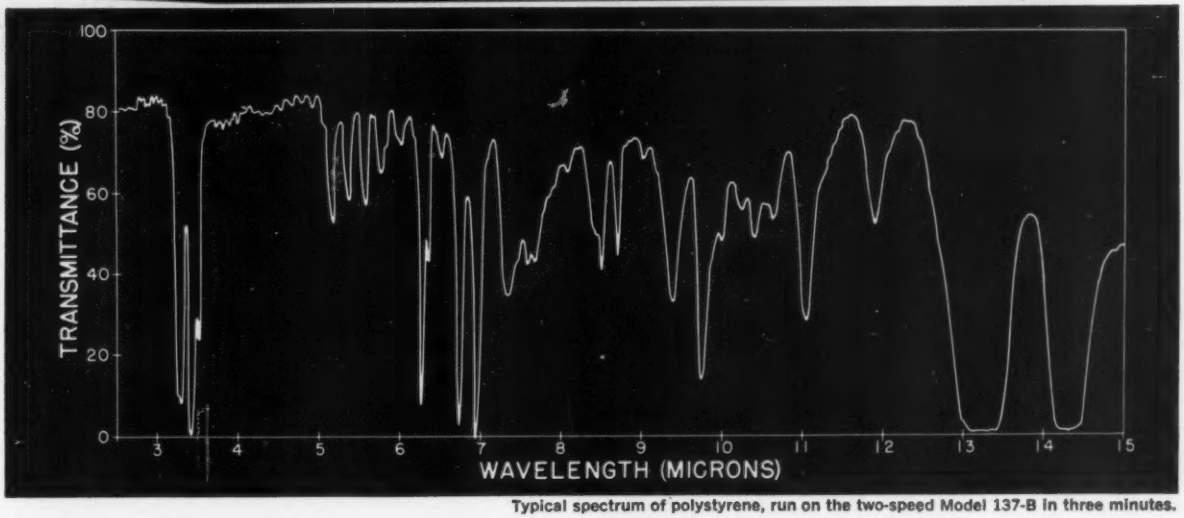

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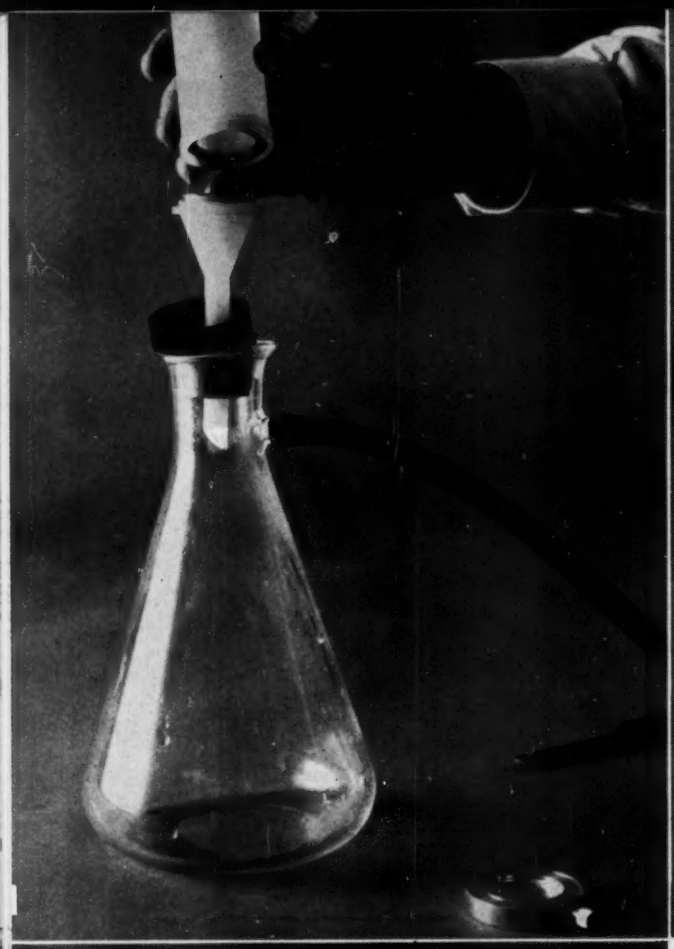

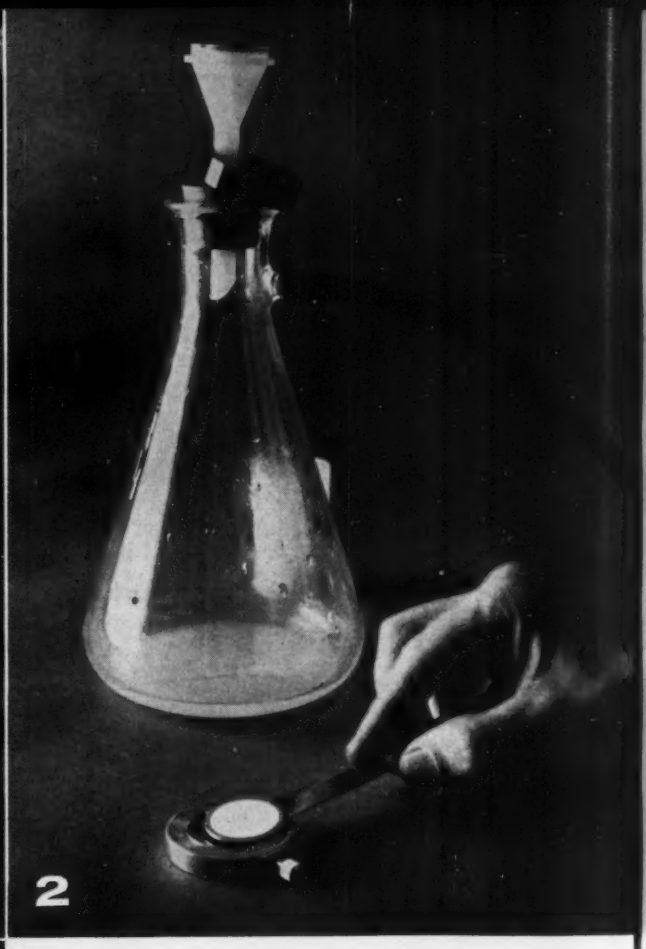

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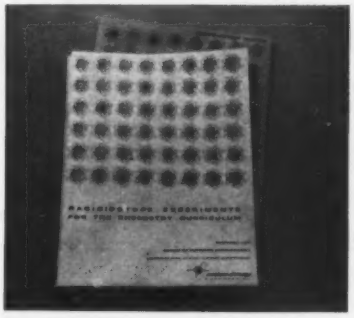

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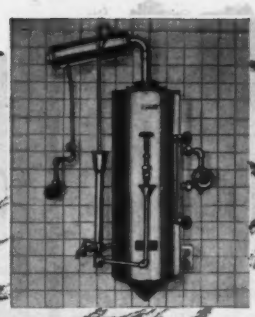

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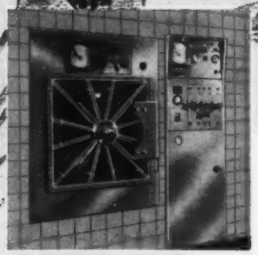

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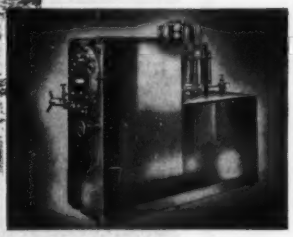

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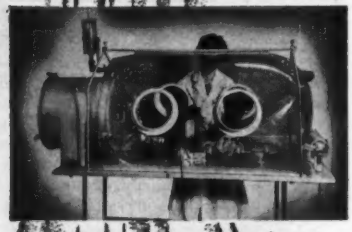

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▶ Labline, Inc., 3070 W. Grand Ave., Chicago 22, Illinois, announces that a new, transistorized thermistor sensing and control circuit has been developed for their Dubnoff Shaking Bath. It presenses and controls any change in temperature within ±0.05°C regardless of the shaking speed.

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▶ A new, budget-priced, 550 watt, magnetic stirrer hot plate is now available from Will Corp., Box 1050, Rochester 3, New York, manufacturers of the popular Will Gyratherm.

▶ A new model (137-B) of its low cost infrared spectrophotometer, which can provide automatically recorded spectra in one-quarter of the time previously required, has been introduced by the Instrument Division of the Perkin-Elmer Corp., Norwalk, Connecticut.

▶ F & M Scientific Corp., New Castle, Delaware, has available a stable dc power supply for gas chromatographs using either thermistor or hot-wire detectors. Model T-300 dg Power Supply converts 105–126 v ac to 12 v dc. The unit connects directly, without modifications, to chromatographic bridge circuits.

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(*Continued on page A253*)

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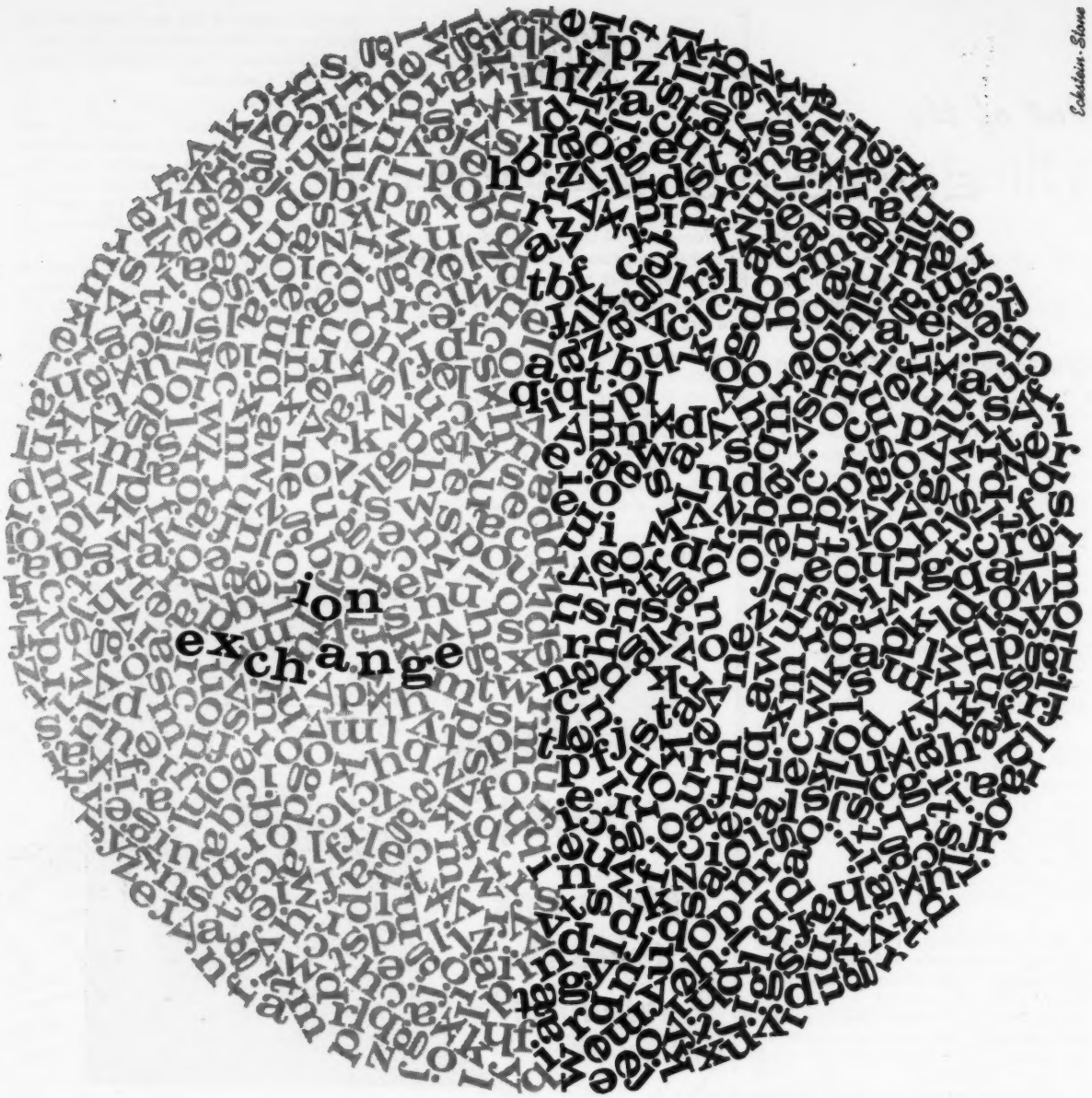

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full visibility of the vacuum chamber interior.

▶ A new rotary spray evaporator, made by Nester & Faust, 2401 Ogleton Rd., Newark, Delaware, gets its effectiveness from a rotating stainless steel spray agitator driven by a constant speed, sparkproof motor, which picks up the solute and solvent and sprays it evenly onto the heated walls of the flask.

▶ Industrial Instruments, Inc., 89 Commerce Rd., Essex County, Cedar Grove, New Jersey, announced availability of the Type RID Differential Conductivity Meter designed to measure, indicate, and transmit to a remote recorder, the difference in solution conductivity at any two locations.

▶ Accropet, a new automatic pipettor for simple, accurate one-hand operation, has just been introduced by the Emil Greiner Co., 20–26 N. Moore St., New York, N. Y.

▶ A jet adapter, now available for converting a CO_2 fire extinguisher to produce a very fine controllable stream of dry ice having a temperature of −109°F, is available from Rolf Darbo, Box 2158, University Station, Madison, Wisconsin.

▶ Comroe Laboratories, Inc., 5208 Lake Park Ave., Chicago 15, Illinois offers "Dip-Chek" conductivity meters designed specifically for the water treatment field.

▶ Palo Laboratory Supplies, 75 Ninth Ave., New York 11, N. Y., has announced an improved model of its popular, automatic glass Pipetter. The new unit offers even greater accuracy than its forerunner according to the company. Now the reproducibility of this handy dispensing device is held to within less than 1% deviation which is equal to that of far more costly pipetting machines.

▶ A glass tipped probe containing a stabilized thermistor is used with standard A + Thermophil instruments to read temperatures of electronic components within 0.2°F. Improperly functioning components and chassis hot spots can be quickly located without danger of shorting out the equipment being inspected. These temperature test instruments are offered for a variety of temperature spans by Atkins Technical, Inc., 1276 W. Third St., Cleveland 13, Ohio.

▶ "Z-racks," a new type stainless steel test tube rack in a variety of sizes, are available from Massey Dickinson Co., Inc., Coker St., at Thayer Rd., Watertown 72, Massachusetts.

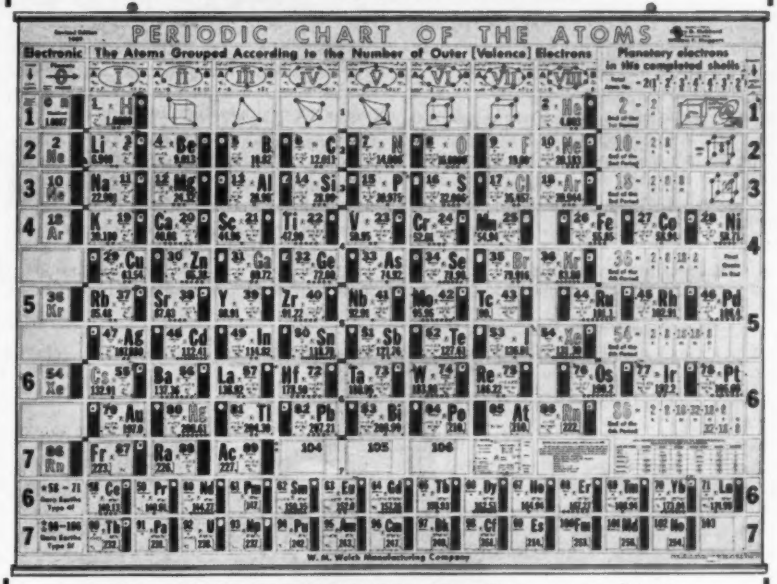
New Literature

● Brothers Chemical Co., 575 Forest St., Orange, New Jersey, offers a descriptive

(*Continued on page A254*)

WELCH CHART OF THE ATOMS
NEW 1959 Edition

Chart and 48-page Key Booklet both completely revised
by Dr. William F. Meggers, National Bureau of Standards


PERIODIC CHART OF THE ATOMS
Electronic
The Atoms Grouped According to the Number of Outer (Valence) Electrons
Planetary electrons in the completed shells
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4854. CHART OF THE ATOMS, 1959 Edition. Each, $7.50
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COMPLETE with pump, remote sampler and one hundred tubes in sturdy leather case.

Don't take chances with poisonous and deadly fumes. This easy-to-use, precision instrument will tell you when dangerous fumes are present . . . down to a few PPM. Send for complete literature.

* MAXIMUM ALLOWABLE CONCENTRATIONS for exposure during an eight hour day adopted at the 22nd annual meeting of the American Conference of Governmental Industrial Hygienists.

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Out of the EDITOR'S BASKET

pamphlet on *Gas Detector Model 60;* this device can be used to identify a variety of toxic gases and vapors.

● Bulletin *#154* describes what is believed to be the most complete line of disposable type demineralizers. Write Barnstead Still and Sterilizer Co., 2 Lanesville Terrace, Boston 31, Massachusetts, for copy of Bulletin *154*.

● Carborundum's pamphlet *Materials for Advanced Technology* is a handy data packed, 8 page, 2 color roundup on 12 new products from the Company's Research and Development Division. Write: Department BMD, The Carborundum Co., P. O. Box 337, Niagara Falls, New York.

● Hammer Electronics Co., Inc., P. O. Box 531, Princeton, New Jersey, has just published a new, illustrated, 40-page catalogue describing nuclear instruments and systems, designed to perform a given counting or analyzing function.

● Extreme heat protection, low temperature flexibility, good electrical properties, resistance to ozone, corona, weathering and thermal shock are just a few of the properties that are enabling silicones to play such a vital role in meeting today's space age requirements. A complete discussion of these properties is available in *CDS-276*, a publication of The Silicones Department, General Electric, Waterford, New York.

● Minneapolis-Honeywell Regulator Co., Wayne and Windrim Ave., Philadelphia 44, Pennsylvania, offers *Catalogue C-15-2a* covering a complete line of "Electronik" controllers, pneumatic and electric.

● Catalog #8, a comprehensive, newly revised, 1,057 page volume, presents detailed information on Nylab's complete line of scientific instruments and apparatus; and includes almost every piece of laboratory equipment commercially available. It is a combination reference-purchasing book containing over 5,000 illustrations, detailed descriptions, specifications, sizes, dimensions, and costs. An extensive cross-reference index of each item under every recognized name and description is also included. To facilitate ordering, Nylab has assigned a specific catalog number to each item and to each size of item, and provides a color-coded identification system throughout this catalog for user convenience. To obtain your copy of the New Nylab Catalog #8, address requests, on your company or institution letterhead and stating title please, to New York Laboratory Supply Company, Inc., Catalog Dept. S, 76 Varick Street, New York 13, N. Y.

● The Matheson Company, Inc., has published an 8 page bulletin, "Sterilizing Gas Mixtures" describing the advantages and applications of Gas Sterilization with Ethylene Oxide Mixtures. The bulletin lists the types of Sterilizing Gases prepared by Matheson, discusses sterilizing procedures and conditions and fumigation. Information is included on handling and storage of gas cylinders, toxicity and First Aid. The Bulletin and Sterilizing Gas Price List, are available without cost from The Matheson Company, Inc., P.O. Box 85, East Rutherford, N. J.

● An informative and well illustrated brochure, entitled "Foresight . . . not hindsight!" describing the NCA Radiation Film Badge Service, is available from Nucleonic Corporation of America, 196 DeGraw St., Brooklyn 31, N. Y. The brochure describes in detail the many features of NCA's Film Badge Service such as its preventive exposure reports, permanent coding system and one badge coverage for X-Ray, isotope and neutron exposure. A Radiation Protection Guide in the form of a wall chart is also available on request.

● The Achema Year Book 1959/1961, European Catalogue of Chemical Plant, Apparatus and Instruments has just been issued. It consists of 1162 pages in four languages, English, French, German and Spanish, edited by H. Bretschneider on behalf of the Dechema Deutsche Gesellschaft fur chemisches Apparatewesen, Frankfurt (Main).

The Achema Year Book 1959/1961 is sent to all personally registered visitors of the Achema Congress 1961 free of charge as representing part of their membership fees.

Continued on page A256))

Gives reproducible results, bottle after bottle

Take one set of results you got with Du Pont Ammonium Hydroxide Reagent. You can change bottles, shipments or locality, and you'll reproduce the same results—time after time! That's because each bottle gets 113 separate analytical tests to keep it uniform for your use.

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Du Pont's family of reagents includes Nitric, Sulfuric, Hydrochloric and Glacial Acetic acids, and Ammonium Hydroxide. They're readily available all over the country. Ask your local laboratory supply house or write for list of suppliers. Industrial and Biochemicals Dept., N-2545JE, Wilmington 98, Delaware.

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FOR PERFORMANCE YOU CAN DEPEND ON

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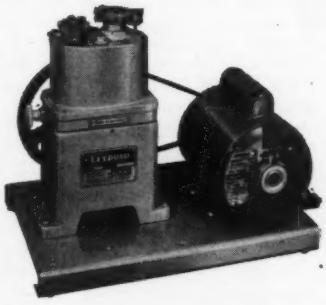
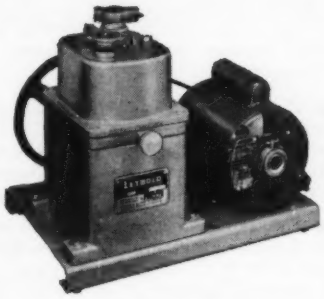


Single-Stage Rotary Vane Gas Ballast Pump
Free Air Speed, 33 liters/minute. Ultimate Vacuum, mm Hg: with gas ballast, 6×10^{-1}; without gas ballast, 2×10^{-3}.
No. CE 352-71, each.....$155.00



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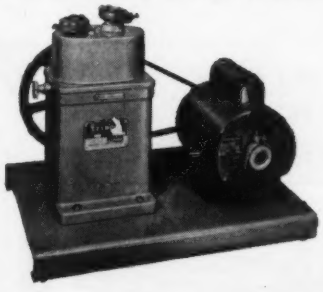

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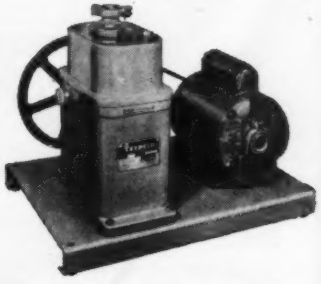
No. CE 352-76, each.....$315.00



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Leybold's *gas ballast* design eliminates the vapor problems you have experienced with conventional rotary vane high vacuum pumps.

When water and other vapors condense in the conventional pump, the oil becomes contaminated; efficiency goes down, pumping time goes up, and the vacuum obtainable is limited. Additional time and money is wasted when replacing the contaminated pumping oil.

WHY VAPOR FORMS IN CONVENTIONAL PUMPS

Oil sealed rotary pumps achieve the remarkably high compression ratio of 760:1 in order to discharge gases removed from the vacuum system. Vapor particles are compressed so compactly in ordinary pumps that they condense to form droplets. Further compression does not increase pressure in the pump chamber, but only forms more droplets. Consequently, the exhaust valve is not forced open by pump pressure, and exhausting does not take place.

HOW THE LEYBOLD GAS BALLAST SYSTEM PREVENTS CONDENSATION

The Leybold gas ballast device draws fresh air from the outside into the pump chamber during the compression stage after the chamber has been shut off from the intake side of the pump. This fresh air (gas ballast) prevents too high a compression ratio of the vapors in the pump, which could lead to condensation of vapors. Excess pressure in the pump required to open the exhaust valve is produced before water particles are compressed and condense. As long as water is present in the vacuum system more vapor is formed and continuously removed.

Leybold rotary gas ballast pumps can be operated with or without gas ballast, as required. They combine the advantages of ordinary oil-sealed rotary pumps with the ability to remove vapors and gases mixed with vapors. After all water vapor has been removed, the pump can be operated without gas ballast to obtain a higher vacuum.

1. The Leybold pump with gas ballast is connected to the nearly evacuated system containing a liquid and its vapor particles.

2. As the pump chamber is shut off from the system, the gas ballast valve opens and air fills the pump chamber.

3. The gas ballast valve closes and the exhaust valve opens. Pressure required to open the exhaust valve has been reached before condensation could take place.

4. Both air and vapor particles are expelled from the Leybold Gas Ballast Pump.

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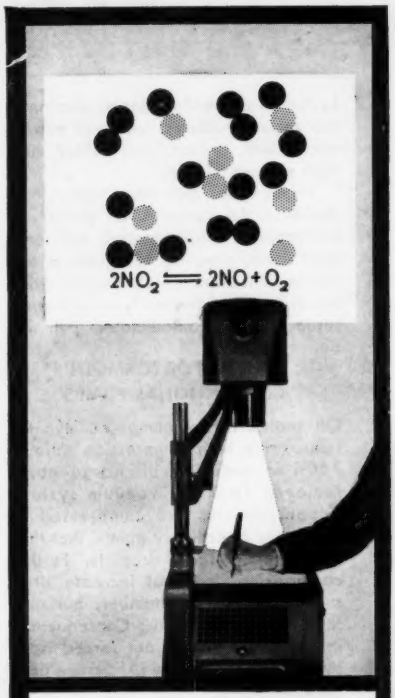

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Out of the EDITOR'S BASKET

● A revised and expanded 16-page catalogue which gives detailed information on the Pyrex Brand "double-tough" drainline has been published by Corning Glass Works, Corning, New York.

● A condensed catalogue of high vacuum components and equipment manufactured by NRC Equipment Corp., 160 Charlemont St., Newton 61, Massachusetts, is now published and available through the firm and its regional sales offices.

● A new single-page data sheet describing the L & N Regulated Voltage Power Supply, which provides constant measuring-circuit current in L & N potentiometer recorders and controllers from the ac line, eliminating battery, standard cell and standardizing mechanism, is now available from Leeds & Northrup Co., 4934 Stenton Ave., Philadelphia 44, Pennsylvania.

● The 41st Edition of *The Handbook of Chemistry and Physics* is now available to students at about one-half price, Chemical Rubber Publishing Co., 2310 Superior Ave., N. E., Cleveland, Ohio.

● The Superintendent of Documents, U. S. Government Printing Office, Washington 25, D. C., offers the following:

Research Highlights of the National Bureau of Standards, Annual Report 1960, National Bureau of Standards Miscellaneous Publication 237, 189 pages, 65 cents.

Precision Measurement and Calibration, National Bureau of Standards Handbook 77, issued February 1, 1961, three volumes: Vol. I, *Electricity* and *Electronics*, 845 pages, $6.; Vol. II, *Heat and Mechanics*, 965 pages, $6.75; Vol. III, *Optics, Metrology, and Radiation*, 1,025 pages, $7.00.

Standard X-ray Diffraction Powder Patterns, by Howard E. Swanson, Marlene I. Cook, Eloise H. Evans, and Johan H. deGroot, National Bureau of Standards Circular 539, Volume 10, issued September 23, 1960, 61 pages, 0.40 cents.

● *May We Help You?* a new booklet describing a wide range of supporting services available for instrument users and potential users, has been published by the Instrument Division, Perkin-Elmer Corp., Norwalk, Connecticut.

● The following reports available to science and industry through the Office of Technical Services, Business and Defense Services Administration, U. S. Department of Commerce, Washington 25, D. C.

PB 161 938 *Research on New High-Temperature Semiconducting Materials.* S. S. Devlin and others, Clevite Corporation, for Wright Air Development Division, U. S. Air Force. June 1960, 157 pages, $3.

PB 161 772 *Toxicity and Personal Decontamination of Boron Hydride Propellant Fuels.* S. Rothberg and others, Army Chemical Center. February 1960, 16 pages. $1.50.

(*Continued on page A260*)

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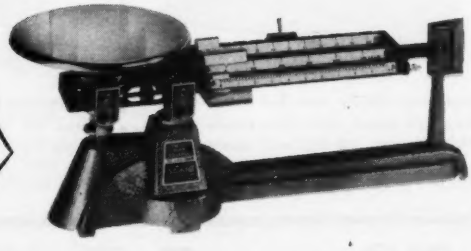

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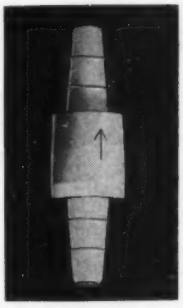

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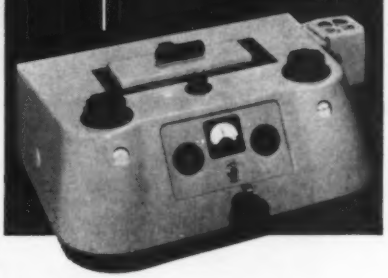

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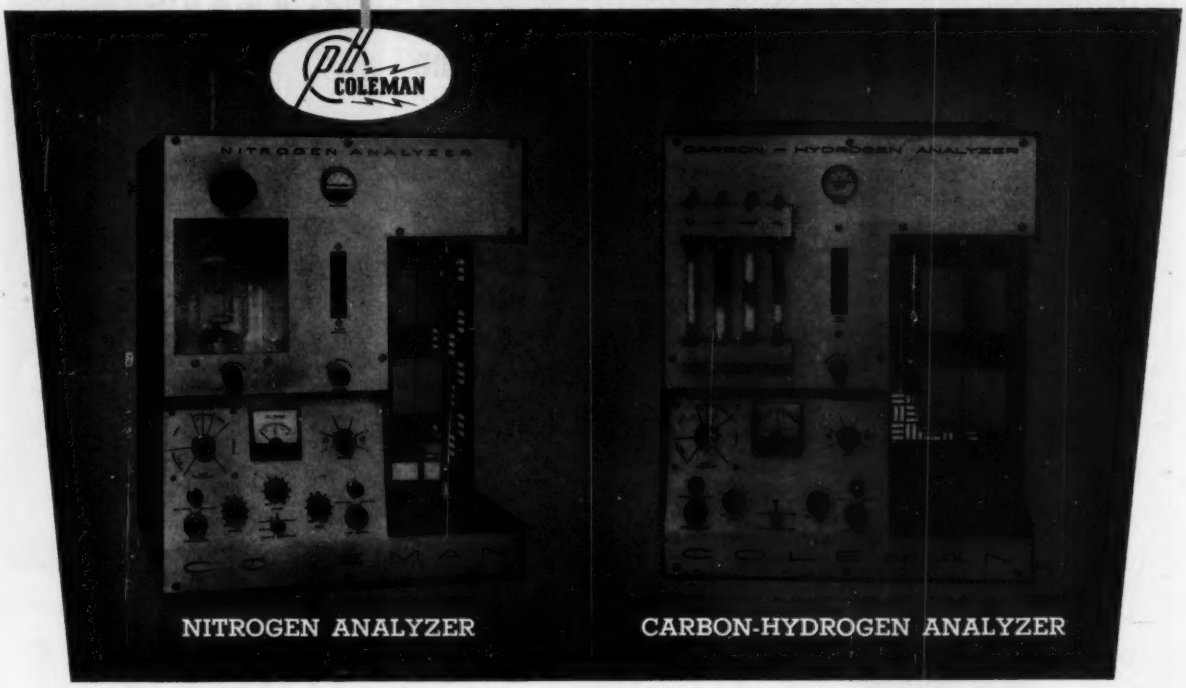

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Automation revolutionizes standard analytical methods

These instruments make a radically new approach to classical analytical chemistry.

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Both instruments perform standard combustion analyses for nitrogen and carbon-hydrogen . . . but they are **COMPLETELY AUTOMATED**. This, for most of us, is revolution enough!

The Nitrogen Analyzer burns the sample and selectively absorbs the combustion products, except Nitrogen. Nitrogen is collected in a micrometer-driven syringe providing direct volume readout in microliters.

The Carbon-Hydrogen Analyzer performs a similar operation. It collects the combustion products of hydrogen (as water) and carbon (as carbon dioxide) in separate absorption tubes which are weighed after each analysis.

Both instruments provide vast improvements in reproducibility over traditional methods . . . variations in operator technique are eliminated as a source of analytical error.

Other important benefits common to both instruments:

SPEED—instrument operating cycle is only 8 minutes.

ACCURACY—results of routine nitrogen and carbon-hydrogen determinations agree with theoretical percentages ±0.2%.

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VERSATILITY—Sample sizes range from 1 to 100 mg; sample substances include virtually all homogeneous materials that burn below 1100° C.

Put automated combustion analysis to work in your laboratory . . . ask your instrument dealer for a demonstration.

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The world's lowest cost, high capacity de-mineral-izer. Faucet connected—water pressure operated. Multi-jet feed. De-ion-izes tap water—fast—up to 2 gals. per min.—120 G.P.H. Use it for immediate volume needs—or intermittently. DEEMAJET® Model 128 complete with resins - $39.50. Extra DEEMINITE® Resin Refill Units-$21.00.

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Fill quart bottle with tap water and invert on holding stand as shown. Operates unattended. Gravity flow—2 to 3 quarts per hour—insures consistent quality. DEEMINAC® Model SD-326 complete with metal stand, graduate and cover—$6.95. Extra Filters (A-6) $4.00. Demineralizer only, without stand; etc. DEEMINAC Model 32-6-$5.75. Other DEEMINAC models from $1.75.

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TRUBORE® Stirrers, pioneered by Ace, feature a variety of well designed interchangeable bearings and rods. TRUBORE® Stirrers are manufactured to closest tolerances to give this outstanding performance: Average leak rate of only 6.4 mm. Hg/min. (unlubricated) at 760 mm. Hg. differential pressure. For lubricated stirrers, leakage is less than 0.05 mm. Hg/min. for the same pressure differential A pressure of 1 mm. absolute is attainable with unlubricated surfaces at speed of less than 100 R.P.M.

The performance, assured by individual gauging and inspection of every component before packing, has made the Ace TRUBORE® Stirrer the most widely used precision glass stirrer in research today. Try Ace TRUBORE® Stirrers. Full information in Catalog 60. Write Dept. J for your copy.

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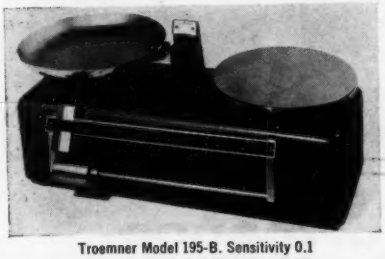
and other improvements make this popular heavy-duty balance better than ever!



Troemner Model 195-B. Sensitivity 0.1 gram; capacity 3 kilograms. $100.

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Newly redesigned for all-around laboratory use, Troemner Models 195-B and 2-89B are now set in a very sturdy aluminum case with chemical-resistant blue-gray finish.

Choose according to desired capacity and sensitivity: Model 195-B has capacity of 3 kg., sensitivity of 0.1 g.; price $100. Model 2-89B has 6-kg. capacity, 0.2-g. sensitivity; price $115.

Weigh beams on both models are graduated either in grams or in ounces. Pans or flat plates are of polished stainless steel. A modern index tower protects the easy-reading pointer. Sliding and locking tare weight.

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Out of the EDITOR'S BASKET

New Chemicals and Reagents

◇ The time required for esterification of fatty acids prior to chromatographic analysis can be shortened by use of BF_3-methanol reagent (*Chem. Eng. News 38*, No. 29, 58 (1960)). With this material complete esterification is accomplished in two minutes. The reagent is available from Applied Science Laboratories, State College, Pennsylvania.

◇ Bio-Rad Laboratories, 32nd and Griffin Ave., Richmond, California, offer *Price List D* of "stable Isotopes."

Nuclear-Chicago Corp., 359 E. Howard Ave., Des Plaines, Illinois, has a kit of five commonly used radioisotopes that can be purchased without a license from The AEC.

Miscellany

★ Macro Models, P. O. Box 287, South San Francisco, California, offers a variety of styrafoam models designed to show bonding, crystal structure, and molecular orbitals. The same company has also magnetic "Macro Discs" designed to show derivation of formulas, electron structures and to demonstrate particle flow in reactions.

★ A research project being conducted by the University of Maryland department of plant physiology is the subject of the cover illustrations and feature article in the latest issue of *Labasco News*. It may be obtained from Labasco, Inc., 401 West St., Charles Rd., Lombard, Illinois.

★ A series of intensive one- and two-week courses for Industrial Scientists in the use of specialized tools in chemistry and physics will be offered this summer by the Polytechnic Institute of Brooklyn. Contact Mrs. Doris Cattell, 333 Jay St., Brooklyn 1, New York, for information.

★ The Pennsylvania State University has established an interdisciplinary curriculum leading to the M.S. and Ph.D. degrees in Solid State Technology. Candidates for degrees will be accepted beginning with the 1961–62 school year. The program was established because present-day proficiency in solid state technology cannot be gained in any one of the traditional disciplines, but must combine work in two or more.

★ *Esso Oilways*, February, 1961, describes the work of the ACS as beneficial not only to chemists and chemical engineers, but everyone living in an industrial society. The article is entitled "Catalytic Agent for the Chemical Profession."

★ Massachusetts Institute of Technology offers the "Technique of Infrared Spectroscopy," July 17–July 21, 1961, and "Applications of Infrared Spectroscopy," July 24–July 28, as part of their special summer program.

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For complete details write Dept. VG for Bulletin 6000

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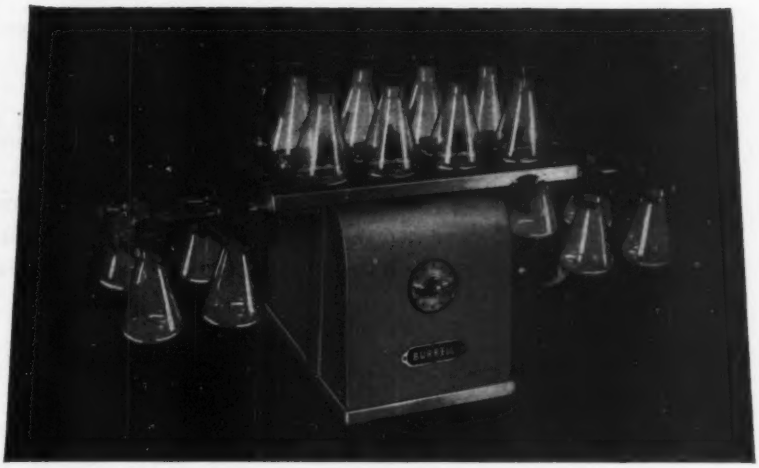

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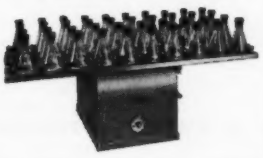

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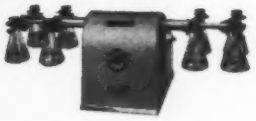

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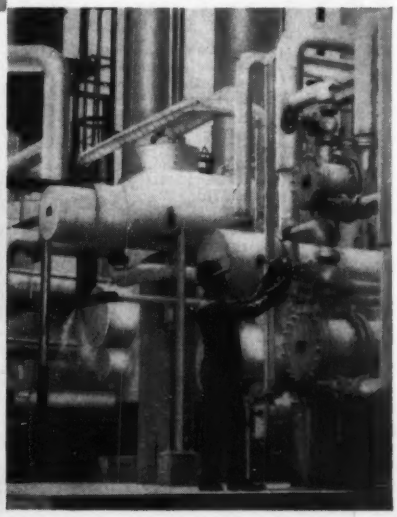


a Chem Ed feature

CHEMICAL PROJECTS

Research Ideas for Young Chemists

Compiled by **JAY A. YOUNG,** Kings College, Wilkes-Barre, Penna.
JOHN K. TAYLOR, National Bureau of Standards, Washington, D. C.

Simple Charles' Law Experiment

See DAMERELL, V. R., *J. Chem. Educ.*, **32**, 534–5 (1955).

The procedure described, requiring only a capillary tube, a thermometer, and an oil bath, is extremely simple. The volume of confined air, approximately proportional to its length in a cylinder of approximately uniform diameter, is determined at two known temperatures. Many refinements are possible: other gases can be used, the error due to the vapor pressure of oil can be minimized or completely eliminated, the non-uniformity of the internal diameter of the capillary tube can be measured and incorporated into the calculations, the precision of measurement can be increased by using a cathetometer or other level-measuring device.

Questions:

When the volumes and temperatures of a fixed quantity of gas are measured with sufficient precision, Charles' Law is not correct. Show from data you obtain in your own experiment that Charles' Law is not correct, or that it is correct within a stated limit of precision.

Make some or all of the refinements mentioned in the abstract above, or devise other refinements. Evaluate their relative effect upon the precision of your measurements.

For any gas you select, does its deviation from Charles' Law increase or decrease as the temperature is lowered, and as the boiling point of the gaseous substance selected is approached?

Can you modify the procedure described and demonstrate the principle known as Boyle's Law without extensive, complicated apparatus?

Can you modify the procedure so that the molecular weight of a volatile liquid can be determined?

Determine the equilibrium constant of the reaction

$$N_2O_4 \rightleftharpoons 2NO_2$$

Meaningful Solubility Studies in Elementary Quantitative Analysis

See RAMETTE, R. W., *J. Chem. Educ.*, **33**, 610–13 (1956).

The solubility product of a slightly soluble compound is not, despite statements in many elementary textbooks, a number whose value is fixed only by the temperature and by the properties of the compound itself. The measured value of a solubility product depends also upon the presence or absence of other solutes in the solution which is in contact with the undissolved portion of the slightly soluble solute. However for practical reasons it is desirable to identify a single, non-varying, value to which the name "solubility product" can be affixed. To achieve this end, it is convenient to ascribe the variability of the solubility product, as measured, to a function called the "activity coefficient."

The primary cause of variation in the value of the activity coefficient can be attributed to variations in the "ionic strength" of the supernatant solution. ("Ionic strength" is an expression which takes into account the effects of all ions present. See a textbook of analytical or physical chemistry for a definition.) In this outstanding paper, Dr. Ramette outlines the experimental and mathematical procedure by which the activity coefficient of calcium sulfate can be determined. The constancy of the calculated solubility product of silver bromate, at constant ionic strength, is demonstrated by another experimental procedure. (This procedure can be modified to show that the solubility product, as calculated, changes in value when the ionic strength is changed.) A study of the solubility of lead sulfate as a function of acidity forms the subject of a third investigation.

No questions need be appended here since the article itself suggests a sufficient number of interesting related studies. However, the series of three investigations described in the article and the additional investigations suggested by the author are probably best suited for a student eligible to undertake work in the Advanced Placement Program now in effect in many high schools.

Verification of the Henderson-Hasselbach Equation

See BLACKWELL, R. Q. AND FOSDICK, L. S., *J. Chem. Educ.*, **31**, 138 (1954).

The most commonly used equation which describes the relationship between the *p*H of a solution and the concentration of acid and conjugate base (or base and conjugate acid) present as solutes in the solution is known as the "Henderson-Hasselbach equation." Usually, this equation is used to calculate the *p*H of a buffer solution from the known quantities of solute added to a solvent (water) and diluted to a known volume. From the known quantities of solute and of volume of solution, and from a measurement of the *p*H of the solution, it is also possible to calculate the ionization constant of the acidic or basic solute. The *p*H may be measured by a *p*H meter, by addition of an indicator and comparison of the color formed with the color of a similar solution of known *p*H, by direct potentiometric measurement, and by other means.

Questions:

Prepare a series of solutions containing known amounts of a weak acid (such as acetic acid) and its conjugate base (acetate ion) and compare the measured *p*H of these solutions with the calculated *p*H.

Prepare a series of solutions containing known amounts of a weak base and its conjugate acid and compare the measured *p*H of these solutions with the calculated *p*H.

Prepare a solution of a weak base and its conjugate acid, or of a weak acid and its conjugate base; measure the *p*H of the solution and calculate the ionization constant of the base or acid, as applicable. As a variation of this, prepare a series of such solutions, plot the data obtained in appropriate form on graph paper, and obtain the ionization constant from the graphical plot.

Any of the above questions can be investigated further by measuring the *p*H in more than one way.

Simulated Research for Freshmen

See SUMMERBELL, R. K., LESTINA, G., KING, L. C., AND NEUMANN, H. M., *J. Chem. Educ.*, **32**, 475–7 (1955).

In this excellent article, the authors suggest that solutions to be analyzed by students could contain an unfamiliar element which is to be identified, along with the more familiar ones. After laboratory study of a standard analytical scheme, the student is given a sufficient quantity of a solution containing an ion of an unfamiliar element for study and laboratory examination. From the knowledge gained and from further library study, the student devises his own qualitative scheme which incorporates the new element along with the usual familiar elements. He then tests this scheme with an unknown which may or may not contain this additional solute.

Questions:

Sommerbell *et al.* suggest the following "extra" elements: Li, Cs, Au, Be, In, Tl, Th, V, Mo, W, U, Pt, Ce, Te. Select one of these, or another not on this list, and after a study of the properties of the selected ion, devise a plausible analytical scheme which includes this element along with the usual elements. Test your scheme to be sure it is satisfactory.

Determine the properties of two or more "extra" elements and devise an analytical scheme suitable for these, along with the more familiar elements. Test your scheme to be sure it is satisfactory. After you have devised a suitable scheme that includes one or more "extra" elements and have decided that your scheme will work, determine the sensitivity of your analytical procedure for the extra elements.

Measure the degree of quantitative separation of the extra element provided by your scheme and its variation in the presence of a few, and of many, of the usual elements. Account for any variation that you find.

Devise a scheme for the analysis of anions which includes one or more unusual anions. Test your scheme to be sure it is satisfactory.

Most analytical schemes utilize selective precipitation and solution as the basis for each separation step. Devise a scheme which uses unusual separative or preparative procedures, such as electrical deposition, gas chromatography, blow pipe techniques, etc.

Separating Calcium and Strontium in Semimicro Qualitative Analysis

See HAHN, R. B., *J. Chem. Educ.*, **30**, 349 (1953).

It is difficult to separate calcium and strontium because the procedures are detailed and are sensitive to the kinds of errors a beginning student is likely to make. However, strontium nitrate is only slightly soluble in concentrated nitric acid whereas calcium nitrate is much more soluble. Hahn's separation is based on this fact.

Questions:

Determine the sensitivity of Hahn's method. That is, what is the smallest ratio of strontium to calcium for which strontium can be separated and identified? Similarly, what is the smallest ratio of calcium to strontium for which calcium can be separated and identified?

Can you devise another procedure which is equally sensitive or more sensitive for the separation and identification of strontium and calcium?

Most qualitative analytical separations depend upon differing aqueous solubilities of the compounds to be separated. Little work has been done in exploiting the differing solubilities of two or more compounds in non-aqueous solvents. Select a pair of substances which are not easily separated by differing aqueous solubilities and devise a separation procedure which is based upon their markedly different solubilities in non-aqueous solvents. (Common non-aqueous solvents include glacial acetic acid, any anhydrous alcohol, benzene, paraffin oil, molten salts, etc.)

Identifying Zinc in the Presence of Nickel and Cobalt

See LEVINE, E. M., AND KRAKOWER, G., *J. Chem. Educ.*, **29**, 437 (1952).

Zincate ion, $Zn(OH)_4^{--}$, is adsorbed by nickel(II) and cobalt (III) hydroxides. These hydroxides are difficult to remove by centrifugation, for small particles tend to remain in suspension; they can be removed by filtration, however. A definitive test can then be made for zinc in the filtrate. Tests for zinc in the centrifugate often yield a black sulfide, due to the presence of the nickel and cobalt.

Questions:

Can zinc be separated from nickel and cobalt when all three are present in the same solution, by a procedure other than the one recommended by Levine and Krakower?

Is it true that zincate ion is adsorbed by particles of nickel(II) or cobalt(III) hydroxide, or is some other phenomenon responsible for the results described in the article?

In this example, the interference of nickel and cobalt with the determination of zinc is due to an unexpected condition, not to similarities in the chemical properties of zinc, nickel, and cobalt. Find three other elements, one of which is sharply different in chemical properties from the other two, but which are not easily separable, and devise a suitable method of separation.

New Qualitative Identification Procedure for Cobalt(II) and Nickel(I) Ions

See YASUDA, S. K., AND LAMBERT, J. L., *J. Chem. Educ.*, **31**, 572–3 (1954).

In the presence of trisodium monothiophosphate, cobalt(II) or "cobaltous" ion forms a deep blue solution which can be used as a definitive indicator of the presence of this ion. Trisodium monothiophosphate can be prepared from readily available reagents, using the procedure described by Yasuda and Lambert.

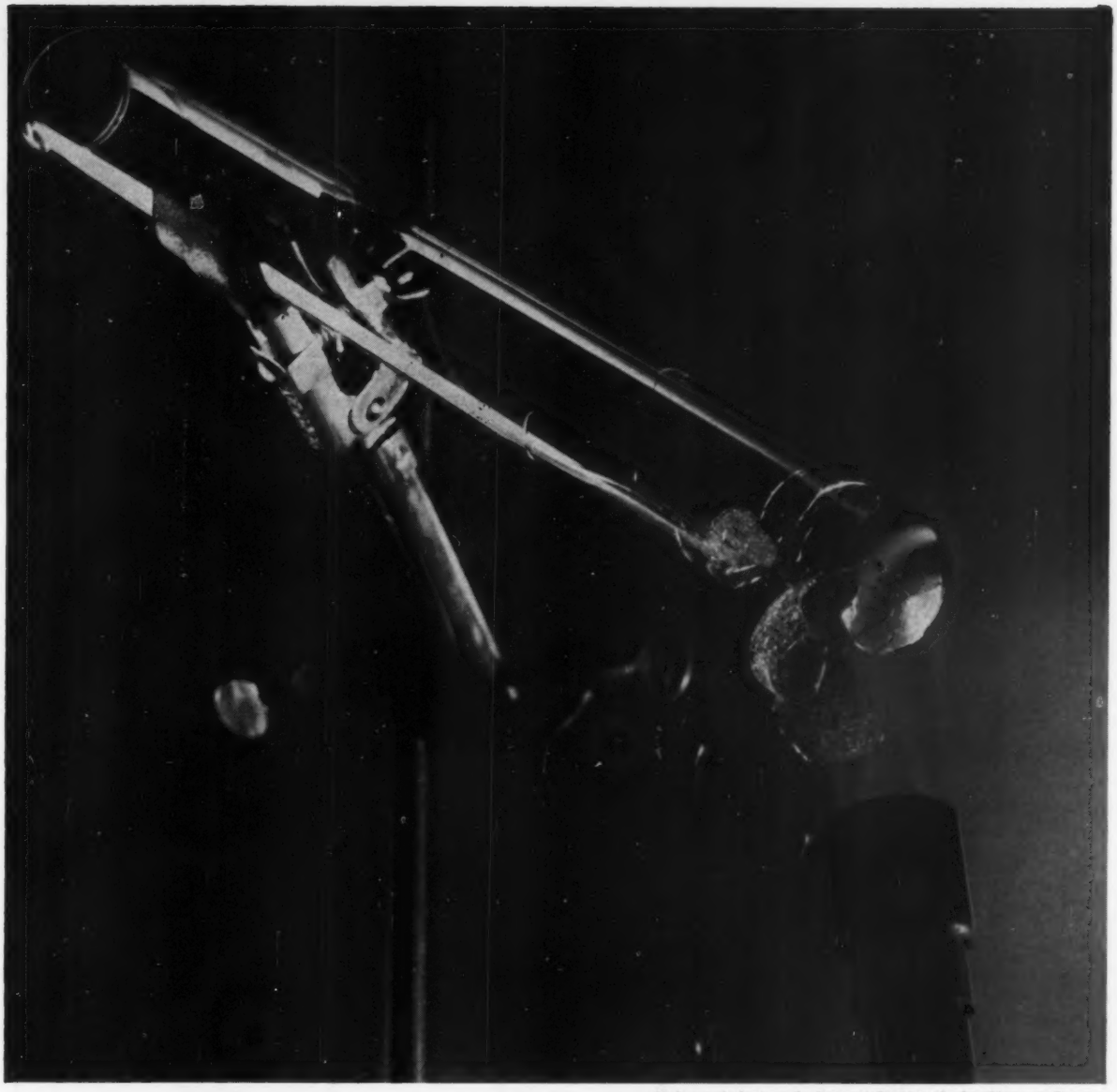
It is probable that many other unfamiliar reagents, with names even more exotic than that of the reagent used here, trisodium monothiophosphate, could be used to identify other ions in an unknown mixture. Clues to the identity of these reagents can be found by diligent study of reference works. When a likely lead is found, the reagent should be tested in the manner indicated in the table accompanying this article.

Questions:

Can you confirm the results described by Yasuda and Lambert? Perhaps, with some alteration of conditions, trisodium monothiophosphate can be used to identify ions other than cobalt(II) ions. Determine the validity of this proposal.

Select, after study of the literature, another unfamiliar compound and show that it can be used to identify one or more ions present in a mixture.

Yasuda and Lambert suggest that the cobalt(II)-monothiophosphate compound is a complex ion rather than a simple salt. Can you confirm this statement?



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ChemEd

EDITORIALLY SPEAKING

Maybe I'll make it through the Science Fair season, but I doubt it!" So ends a letter from a correspondent whose lot it is to receive and try to answer letters from students to a leading manufacturer of chemicals. The fact that sometimes our office walls have heard the same lament and that conversations with other chemists in universities and industry have echoed the same sentiment leads us to use this page to try to stab an octopus.

First we should set the record straight that we are not advocating the abolition of science projects for students. We applaud the principle and endorse with vigor the idea that students use their energies to translate imagination into investigation. The feature "Chemical Projects" now running each month in THIS JOURNAL is an attempt to put the emphasis where we feel it belongs. What we shudder to see is the distortion of this good idea that has often resulted when a poor teacher assumes that this job is done when he assigns a project.

Our correspondent wonders if we are not getting "science project happy" in our schools. Do science teachers know what a project really is? Most pertinent of all, "Do the teachers orient the students properly for doing a project?" His examples point up his questions:

A fifth grade student in a public school was told to make a sundial as a science project. No instructions were given as to how to proceed. She spent one afternoon laboriously crayoning the face of a clock showing 1 through 12 hours, and then asked her father where she should place the two upright pieces.

I receive many requests for help from students that are stupid, ill-conceived and impolite. "Send me all you know about chemistry (chemicals, drugs, sodium compounds, etc.)." "Send me all your information on analytical chemistry (or any other branch of science you can name)." "Send me something on acids (bases, salts, antifreezes. . .)." "Send me all you have on phenol (or any compound, important or rare)." Further, the student is often demanding and insists that we "hurry" as he must turn in his project next week.

Many such requests should never have been permitted by the teacher. I rarely receive requests from teachers asking what information might be available of value to their students. Further, teachers show no imagination (or control) in suggesting the companies to which students write. It looks as though they seldom direct students to libraries as a first source of information. Some appear to hold that if a student has reaped a supply of x number of industrial brochures and booklets by sending out postal cards, he has learned something.

Another problem is that an educator or scientist will give a talk somewhere (or a paper will appear in a relevant educational journal) suggesting a particular area for a science fair project, and the teachers hop on the bandwagon. Case to point: Somewhere nearby, projects in crystal growth and chemical microscopy must have been mentioned recently at a meeting or in a publication. The result has been a flood of requests: "How can I grow large crystals?" "Send me some crystal experiments." "Send me what you know about crystals." "Send me some crystals."[1]

Our own file is thick with similar correspondence (usually forwarded from the business or advertising offices of THIS JOURNAL):

Please give me the equations and the instructions for making all the plastics.

I would appreciate any free literature and samples pertaining to enzymes.

Please send me any pamphlets, literature, and samples in regard to the subject of the coagulation process of producing synthetic fibers. . .P.S. I will gladly accept any material indirectly related to this subject.

Please send me pertinent literature concerning the Hydrogen Bond. I will use this for a research project so please use your discretion in sending me literature that will be most useful to me.

Even having made allowance for the perverse independence of teen-agers, we seriously doubt that the teachers of these students had given rudimentary instructions in how to search for information. We can answer students politely, usually citing references to articles in this Journal located with the aid of cumulative indexes or the collected volume of Tested Demonstrations. We doubt if we could maintain our politeness with some of their teachers. We know we could not be polite with school superintendents who insist that a chemistry teacher have every one of the students in his six classes do a project but refuses to equip either laboratory or library with the necessary resource material.

Maybe all we have done is to get a load off the collective chests of those who want most to help genuinely-interested, adequately-instructed budding scientists. We would like to go further to make one concrete suggestion: Every course labeled "Teaching Methods in Chemistry" that carries education credit should require the prospective teacher to complete several "Science Fair" projects without the use of a postage stamp.

[1] EDITOR'S NOTE: Teachers of crystal-growers *must* know of the PSSC jewel, "Crystals and Crystal Growing," by Alan Holden and Phyllis Singer, available to secondary school teachers and pupils through Wesleyan University Press, Columbus 16, Ohio. It is also an Anchor Book (Doubleday & Co., Garden City, N. Y.).

A ChemEd SYMPOSIUM

Recent Advances in Inorganic Chemistry

Introduction

Inorganic chemistry stands as one of the oldest of the divisions of chemistry, yet it has not always received the veneration and respect which its age might suggest. Except for the classical work of Mendeleff and Alfred Werner, theories and correlative schemes for handling the data from inorganic systems have developed slowly. At one period the subject was accused of being empirical and less stimulating than its sister areas. Fortunately, however, during the past 30 years a number of far reaching theoretical advances have done much to correlate large areas of inorganic chemistry and to convert it into one of the most stimulating of all research areas. Coupled with the theoretical advances have been great advances in the experimental aspects of the subject. Classical experimental problems have been solved. The rare earths can be separated with relatively little human effort, zirconium and hafnium can be separated, the boron hydrides can be synthesized in tonnage lots, fluorine can be handled in large quantities, and certain of the elements can be prepared in a state of purity undreamed of 60 years ago. Even the alchemists' dream, the transmutation of elements, has been realized and new elements can be prepared. Each of these developments has, in turn, spurred further advances in the subarea concerned.

Because of these rapid advances, the educational literature cannot keep up with developments in the field and many stimulating new ideas are buried in the technical journals before they can be incorporated into the college curriculum. To render less probable such an unfortunate development, the Division of Chemical Education and the Division of Inorganic Chemistry of the ACS sponsored a joint Symposium in Cleveland during the April 1960 meeting entitled, "Recent Advances in Inorganic Chemistry." The papers, presented by distinguished chemists, were aimed at college teachers of inorganic chemistry. The large audiences at all sessions indicated a very general interest, both academic and industrial, in the areas covered.

The symposium started with a review by William Lipscomb of theoretical developments associated with the so-called "Electron Deficient Molecules." Since this topic has been the subject of a number of recent papers by Dr. Lipscomb, the work is not published here. A discussion of "Ligand Field Theory" by Ralph Pearson and a paper on the "Mechanism of Oxidation-Reduction Reactions" by Fred Duke completed the more theoretical introduction. The borderline areas lying between organic and inorganic chemistry were covered by: F. Albert Cotton, "Organo Metallic Compounds"; H. C. Brown, "New Selective Reducing Agents"; and Charles B. Colburn, "Recent Developments in N—F Chemistry." Only the last two papers of this group are published here; the first topic has been treated elsewhere.

In the third and final session emphasis was directed toward the inner transition elements. The first paper, by Therald Moeller, was "The Rare Earths—Solved and Unsolved Problems"; the second, by Albert Ghiorso, was "Modern Techniques in New Element Research"; and the third, by Otto Forchheimer and Terry F. Newkirk, was "Recent Advances in Solid State Inorganic Materials." Only the last paper of this trio is presented here.

Certainly the exciting aspects of inorganic chemistry, which were so capably reviewed by the symposium participants, will lead to an even greater development of this, the oldest branch of chemistry.

R. W. Parry, *Chairman of the Symposium*

EDITOR'S NOTE: The annual indexes of THIS JOURNAL usually have a long list of entries under *Inorganic Chemistry*. Many of these papers are appropriate to the "Recent Advances . . ." theme. Readers' attention is called to the following from recent years:

Symposia: "Instruction in Inorganic Chemistry," **36,** 441–468, 502–518 (1959); "New Elements," **36,** 2–44 (1959); and "Inorganic Nitrogen Compounds," **34,** 537–561 (1957).

Reviews: "Inorganic Polymers," **37,** 2, 86, 134 (1960); "Species in Aqueous Solution," **33,** 152, 223, 282 (1956); "Ferrocene," **34,** 268 (1957); "Cyclopentadienyl Compounds," **37,** 568 (1960); and "Ligand Field Theory," **37,** 498 (1960).

Reprints of Sutton Article on Ligand Field Theory Available

Requests for reprints of the article "Some Recent Developments in the Theory of Bonding in Complex Compounds of the Transition Metals," by Professor Leslie E. Sutton of Magdalen College, Oxford University, England [THIS JOURNAL, **37,** 498–505 (1960), October] have far exceeded the original supply. We are departing from usual policy to serve this demand.

Copies of this 8 page article will be sold by the Editor's office. The price is 25 cents per copy on orders up to five copies, 20 cents per copy for orders of five or more. Orders will be acknowledged only if accompanied by pre-payment. Order from: The Editor, Journal of Chemical Education, College of Wooster, Wooster, Ohio.

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Oxidation Reduction Mechanisms

During the past twenty years, and particularly since 1945, the field of oxidation mechanism studies has been a busy one, and enough is now known concerning such mechanisms that the information may well be incorporated into oxidation-reduction theory as it is taught to undergraduates. Inclusion of mechanistic along with thermodynamic theory in this area adds spice and interest to the subject for most students.

When one is considering electron transfer from one particle to another, it is fair to ask how the electron makes its move; since the electron may be credited with no senses, it is immediately clear that an easy path must be provided for the transfer. In most of the cases which have been studied, this path is provided through close association of the oxidant and reductant, the bond between them being of the Lewis acid-base variety. In other cases, the electron apparently is able to penetrate a thin-skinned insulation in moving from reductant to oxidant upon collision. These situations will now be considered in turn.

Reactions Involving a Cation and an Anion

The simplest mechanism of electron transfer involving the acid-base properties of the reactants is that in which a cation reacts with an anion. Cations, particularly those of variable valence, are generally Lewis acids and anions are Lewis bases. After the bond between them is formed, intramolecular electron transfer is provided for by the bond. Some examples of this type of reaction are shown in Table 1. In the case of the Mn(III)-oxalato reaction (*3*), three complex ions are formed: the mono-oxalato, the dioxalato, and the trioxalato manganate ions. All of these ions acts a intermediates; however, the electron transfer rate is much reduced as the number of oxalate ions in the complex is increased. Consequently the reaction slows down as the oxalate ion concentration increases, either by the addition of the ion or by increasing the *p*H to convert oxalic acid to oxalate ion. A similar situation occurs in the cerium(IV) oxidation of glycols (*5*). Again, the complexes with the greatest number of glycol molecules allow slowest electron transfer; *p*H has no effect here, because the glycol is complexed as the molecule rather than as glycolate ion. The intermediate in either of these situations following electron transfer is a free radical since only one electron is transferred. The probability is that this free radical is an oxalate ion minus an electron, $\cdot C_2O_4$ in the one case, and the radical RCHOH plus RCHO in the other. Such radicals may be studied through reactions which they induce in normally unreactive substances placed in the solution (*17*). [Such reactive intermediates have been called *reactates* (*18*). The chemistry of reactates is not well studied and deserves much more work; their importance is emphasized by the realization that probably most oxidations would not proceed if reactates of moderate energies did not exist.]

In the case of the Fe(III)-I^--reaction, the acid base intermediate may be FeI_2^+ or $FeI(OH)^+$, but not FeI^{++} (*1*). Apparently the radical ions I_2^- or IOH^- have much lower free energies than the bare atom, I. In general, when halide ions are oxidized by one-electron oxidants, the reaction involves two halide ions leading to the electron-transfer intermediate, X_2^-, where X is a halogen. Reactions of this sort, then, tend to be higher than first order in halogen. Another example of this effect is in the cerium(IV) oxidation of chloride (*19*), where $CeCl_3^+$ is an important intermediate.

The cation may be either oxidant or reductant. For example in the case of the perchlorate oxidation of titanium(III), it is believed that weak complexes of cation and anion are formed prior to electron transfer (*4*).

Reactions Between Two Cations

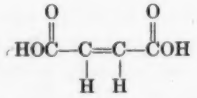
Cations cannot bond directly, being acidic, but two cations may combine with a single base provided the base has two or more electron pairs available for such bonding. Complexes of this type have been shown to be responsible for some electron transfer reactions and are believed to be quite generally involved in reactions between two cations. Examples are shown in Table 1.

The first proof of existence of a basic bridge between two cations was accomplished by Taube and his coworkers (*8*). They chose as oxidant, $Co(NH_3)_5Cl^{++}$ and as reductant Cr^{+2}. Co(III) and Cr(III) both have the property of exchanging ligands very slowly with substances in solution (*20*); thus, one could be sure of the position of the chloride ion before and after the reaction. Before reaction, it was certainly attached to cobalt; after reaction, it was shown to be attached to chromium. The fact that both cations were attached at the same time to the chloride was proven by placing radiochloride in the solution and finding no radiochloride attached to Cr(III) at the end of the reaction (*8*); it is hardly conceivable that the transfer of chloride from Co(III) to Cr(II) could have occurred without exchange unless both cations were attached to the same chloride ion. Incidentally, ammonia does not act as a bridging group because it has available only one pair of electrons and is indeed a very poor electron-transfer bridge.

Presented as part of the Symposium on Recent Advances in Inorganic Chemistry, sponsored jointly by the Divisions of Inorganic Chemistry and Chemical Education, at the 137th Meeting of the ACS, Cleveland, Ohio, April, 1960.

Bases other than chloride ion were tested for their efficiency as bridges in the Co(III), Cr(II) reaction. In order of decreasing effectiveness, the bases were found to arrange as follows: $CN^- > Br^- > Cl^- > SO_4^{-2} \cong H_2O > NH_3$ (*9*). Recently, H_2O was shown to be a true bridge, apparently through use of all four electron pairs on oxygen (*23*).

In further work, Taube and his students showed that conjugated double-bonded systems acted very effectively as electron transfer bases. For example, fumaric acid,



allowed much more rapid electron transfer than did succinic acid, the latter being no better than acetic acid (*21*). The fact that the addition of hydrogen ion increased the rate at which fumarate ion allows electron transfer was attributed to the fact that the use of the acid molecule, rather than fumarate ion as bridge, forces the cation to be bound to the double-bonded oxygen providing better electronic conduction between cations along the chain. It was further shown that *p*-phthalic acid is an excellent electron bridge (*22*); in all cases the bridge in the beginning is attached to cobalt, and at the end of the reaction is attached to chromium. To prove that Co(III) and Cr(II) had hold of opposite carboxyl groups rather than the same one during electron transfer, one of the carboxyl groups was replaced by an aldehyde group. This molecule, when still containing the conjugated system, is a good electron transfer agent; however, the aldehyde group does not stay with the chromium(III), being subject to ready replacement by a water molecule. When the aldehyde is used, no organic complex of Cr^{+3} results.

In more recent experiments, using fumaric acid as a bridge in the Co(III)-Cr(II) reaction and using D_2O as solvent, it was found that some exchange of D for H occurred on the carbon—hydrogen bonds (*24*). In some respects, this is most easily explained by assuming that the electron spends sufficient time in the bridge so that the organic molecule has the properties of a free radical and may add and lose hydrogen or deuterium. Thus, it appears that the electron may be traced to a certain extent as it progresses through the bridge.

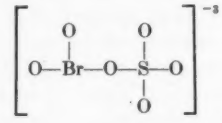
Other reactions which are believed to include bridges of this sort are electron exchanges between Fe(III) and Fe(II) (*12, 13*), Tl(I) and Tl(III) (*25, 26*), Eu(II) and Eu(III) (*11*), and a number of other reactions of this type which must be traced radiochemically. Some reactions using bridges which involve two different elements are the Fe(III)-Sn(II) reaction (*7*) and the above mentioned Co(III)-Cr(II) reactions.

Table 1. Intermediates in Selected Examples of Oxidation Reduction Reactions

Oxidant	Reductant	Intermediate	Reference
Fe^{+3}	I^-	FeI_2^+, $FeIOH^+$	(*1*)
Mn^{+3}	$C_2O_4^-$	$MnC_2O_4^+$, $Mn(C_2O_4)_2^-$ $Mn(C_2O_4)_3^{-3}$	(*2, 3*)
ClO_4^-	Ti^{+3}	$TiClO_4^{+2}$	(*4*)
Ce^{+4}	$CH_3CHOHCH$-$OHCH_3$ (G)	CeG^{+4}, CeG_2^{+4}	(*5*)
Cu^{++}	CN^-	$Cu(CN)_4^{-2}$	(*6*)
Fe^{+3}	Sn^{+2}	Fe—Cl—$SnCl_3^+$ $FeOHSnOH^{+3}$	(*7*)
Co^{+3}	Cr^{+2}	Co—X—Cr where X is OH^-, SO_4^-, Cl^-, Br^-, CN^-	(*8, 9*)
Ce^{+4}	Ce^{+3}	Ce—X—Ce; X is F^-, Cl^-, OH^-	(*10*)
Eu^{+3}	Eu^{+2}	Eu—Cl—Eu^{+4}	(*11*)
Fe^{+3}	Fe^{+2}	Fe—X—Fe, X is OH^-, Cl^-, HOOC⟨⟩COOH	(*12, 13*)
NO_3^-	HSO_3^-	$HON(SO_3)SO_3^{-2}$ $(HO)_2NSO_3^-$	(*14*)
BrO_3^-	HSO_3^-	O_2Br—O—SO_3	(*15*)
MnO_4^-	MnO_4^{-2}	MnO_4—M—MnO_4^{-2} · where M^+ is alkali metal ion	(*16*)

Reactions Involving Anions Only

Although anions are primarily basic in the Lewis sense, acidic properties are also exhibited by many anions, either by accommodation of more than four electron pairs by the central element of the anion, or by displacing other bases normally part of the anion. For example, in the reaction between bromate and sulfite (*15*), the intermediate appears to be



where the sulfur accommodates five electron pairs and the sulfite acts as a base; this is proved by using bromate containing O^{18} and finding that the resulting sulfate contains one oxygen in four of those originally part of the bromide ion. Again, it is not considered possible that the bromate oxygen could be transferred to the sulfur without exchange with solvent unless both Br and S had hold of the oxygen simultaneously.

Another example is that of the nitrite-sulfite reaction (*14*). In this case, the sulfite ion acts as a base and in the presence of hydrogen ion, displaces hydroxyl ions from the nitrite:

$$HSO_3^- + HONO \xrightarrow{[H^+]} ONSO_3H + H_2O;$$

$$ONSO_3H + H_2O \rightarrow \begin{matrix} HO \\ HO \end{matrix} NSO_3H.$$

This is followed by further displacement of hydroxyl by sulfite until either nitrilodisulfonic acid or nitrilotrisulfonic acid is formed, and upon hydrolysis, sulfate and either hydroxylamine or ammonia are formed.

The halate-halide reactions have been studied and are believed to involve $HOXO_2$ and X^- as follows:

$$HOXO_2 + H^+ \rightarrow H_2OXO_2^+; \; H_2OXO_2^+ + X^- \rightarrow X_2O_2 + H_2O$$

The further steps depend upon the nature of X^-, but it is evident that the base, X^-, has displaced the base, H_2O, from the oxidant in the process of the reaction (*27, 28*).

One recently studied reaction of interest is the electron exchange between MnO_4^{-2} and MnO_4^- (*16*). It has been found that alkali cations apparently intervene, possibly as a bridge, between the two anions. For instance, the reaction is faster in the presence of Cs^+ than in the presence of Na^+, and as Cs^+ is substituted

for Na^+, the rate increases linearly with the Cs^+ concentration. There may be an intermediate or activated complex of the type $MnO_4^- - M^+ - MnO_4^{-2}$.

Reactions Not Involving Acid-Base Properties

There are a number of reactions which proceed readily and yet do not fall into any of the classes discussed above. For example, the electron exchange between ferrocyanide and ferricyanide proceeds at a greater rate than the cyanide exchange; thus, there can be no removal of cyanide ligands in the reaction (*29*). Similarly, the rapid reactions of the 1–10 phenanthroline complexes of Fe(II) and Fe(III) and similar complexes cannot be explained on the basis of acid-base properties of the ions (*30*, *31*). It appears that here we have complex ions containing unsaturated and conjugated systems such that the electron can get very close to the outside boundary of the ion. Further, such ions are weakly solvated so that collisions usually involve the ion directly with no intervening water molecules. In such cases, the insulation between particles becomes very thin and the electron may make its way through from one particle to another without difficulty. This type of reaction at present is best explained on the basis of quantum mechanical tunneling, the latter phenomenon being responsible for electron transfer (*32*). In general, it may be stated that if the electron can be involved close enough to the outer boundary of the particle, transfer is probably due to the thin electrical insulation between particles.

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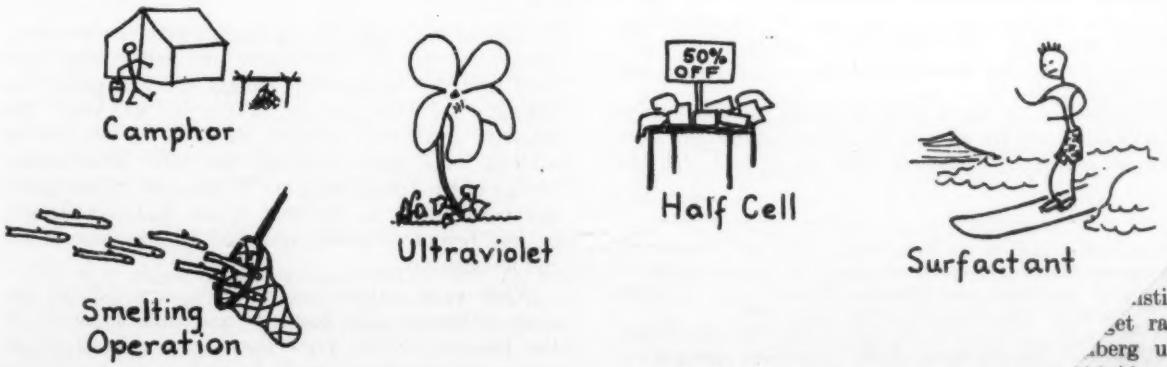
Chem Gems



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Ralph G. Pearson
Northwestern University
Evanston, Illinois

Crystal Field Theory and Substitution Reactions of Metal Ions

A recent article in THIS JOURNAL (*1*) has discussed the newer theories of chemical binding in complexes of the transition metal ions, including crystal (or ligand) field theory.[1] It is our purpose to illustrate the use of this theory in studying substitution reactions of compounds of the metal ions.

Substitution reactions in inorganic chemistry include the replacement of one ligand (*Y* and *X*) by another in a coordination complex, or one metal ion (*M* and *M'*) by another. Following the terminology of Hughes and Ingold developed for organic reactions, these can be called S_N (*nucleophilic*) and S_E (*electrophilic*) reactions respectively.

$$Y + M{-}X \rightarrow M{-}Y + X \quad S_N \tag{1}$$

$$M' + M{-}X \rightarrow M'{-}X + M \quad S_E \tag{2}$$

It is convenient to exclude those substitution reactions which involve changes in oxidation number. With this proviso, substitution reactions become generalized acid-base reactions in which the metal ions (or positively charged central atoms in general) play the role of the Lewis acids and the ligands are the bases. Reactions of the proton are a special subdivision of the general category.

While S_E reactions are known, as in the reaction of Hg^{2+} with $Co(NH_3)_5Cl^{2+}$, they are less important than S_N reactions. Two fundamentally different paths for the latter reaction can be visualized, the familiar S_N1 (dissociation) and S_N2 (displacement) mechanisms. In addition, several other rather restricted mechanisms are likely in certain cases, but the greater part of the effort expended in studying substitution reactions of complexes has been concerned with trying to assign S_N1 or S_N2 labels. This is a difficult task at best since unequivocal evidence is hard to obtain. The strongest evidence would undoubtedly be the detection of the intermediate of reduced coordination number, M, which is characteristic of the S_N1 mechanism.

$$M{-}X \rightleftharpoons M + X \tag{3}$$

$$M + Y \rightarrow M{-}Y \tag{4}$$

However, the nature of M is generally such that it escapes detection by any direct means; subtle evidence for its presence or absence must be judged. In the S_N2 mechanism, a species is formed of increased coordination number, in which X and Y are bonded to M (Y—M—X). This may be an activated complex (very unstable) or an intermediate (some stability).

In spite of the difficulties, the division mentioned above has been fruitful and a general discussion of the effect that changing variables can have on the rates and mechanisms, S_N1 or S_N2, of the reactions of complexes can be given. The variables that might be considered include the nature of the metal ion, the nature of the ligands, the nature of the external reagent, and the geometry and coordination number of the complex. To proceed, it is necessary to have a theory of energetics and binding in coordination compounds, so that differences in energy between the initial state and possible transition states may be estimated at least roughly. A very simple and remarkably useful theory is the old electrostatic one (*2*). This theory is most reliable for systems containing a positively charged central ion and charged or polar ligands where π-bonding (double bonding) is not an important factor.

For example, the coordinate bond energy is defined as the heat of the following reaction in the vapor state.

$$ML^{m+}(g) \rightarrow M^{m+}(g) + L(g) \tag{5}$$

Experimentally coordinate bond energies range from about 15 kcal per bond in a complex such as $Rb(H_2O)_6^+$ to about 500 kcal per bond in $TiCl_4$. It is indeed remarkable that in simple cases, such as those given, a point-charge electrostatic model will give theoretical bond energies in agreement with the experimental ones over such a wide range.

In solution one can only determine differences in coordinate bond energy as one ligand is replaced by another, e.g.,

$$Co(NH_3)_5Cl^{2+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + Cl^- \tag{6}$$

$$Zn(H_2O)_4^{2+} + 4NH_3 \rightarrow Zn(NH_3)_4^{2+} + 4H_2O \tag{7}$$

Because of the compensating effect of solvation energies, it turns out that such differences are rarely greater than 5–10 kcal per bond even though the gas phase coordinate bond energies may differ by 100 kcal. To estimate activation energies for rates of reaction in solution, one must evaluate the total electrostatic energy of the transition state in which an extra ligand has been added in the case of an S_N2 mechanism, or one ligand is partly removed in the case of an S_N1 mechanism.

While exact calculation becomes very difficult because of the irregular geometry and variable nature of the ligands, certain predictions on the basis of an electrostatic model can easily be made as to the relative tendencies towards S_N1 and S_N2 processes as the sizes

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Presented as part of the Symposium on Recent Advances in Inorganic Chemistry, sponsored jointly by the Divisions of Inorganic Chemistry and Chemical Education, at the 137th meeting of the ACS, Cleveland, Ohio, April, 1960.

BrO_3^-, MnO_4^-

[1] The convention that is widely used is that the name crystal field theory applies to the primarily electrostatic approach and ligand field theory to the combined electrostatic and molecular orbital theory in which some covalent bonding is allowed for.

and charges of the various species are changed. Table 1 shows these predictions. By any mechanism one may expect a slowing down of the rate as the charge of the leaving group increases and the size diminishes. This is in good agreement with what is found experimentally. Also as the size of the central ion diminishes and its charge increases, it may be expected that the rate of reaction by any mechanism will decrease. This is indeed found generally to be the case. It is significant that rates of substitution reactions of univalent cations have not been measured as yet, rates of reaction of labile divalent cations can be measured by special techniques to be discussed below, and the slower rates of reaction of many trivalent cations, even the labile Fe^{3+}, can be studied by more conventional techniques.

Table 1. Effect of Charges and Sizes on Rates of S_N1 and S_N2 Reactions

	S_N1 rate	S_N2 rate
Increased positive charge of central atom	Decrease	Opposing effects
Increased size of central atom	Increase	Increase
Increased negative charge of entering group	No effect	Increase
Increased size of entering group	No effect	Decrease
Increased negative charge of leaving group	Decrease	Decrease
Increased size of leaving group	Increase	Opposing effects
Increased negative charge of other ligands	Increase	Opposing effects
Increased size of other ligands	Increase	Decrease

An electrostatic theory using point charges, or uniformly charged spheres, cannot be taken as a complete explanation for the behavior of complex ions, however. For example, the reactivity of iron-(III) complexes compared to the inertness of those of cobalt(III) must be explained, as must the differences between the various transition metal ions and between the transition and non-transition ions in general.

Rates of Exchange: Experimental Data

As an example let us consider some interesting ligand exchange data shown in Table 2. These were obtained (*3*) by using the optically active chelating agent 1,2-propylenediamine tetraacetic acid, H_4PDTA. This is a quinquidentate- or sexadentate- (occupying five or six coordination sites) ligand exactly like the well-known ethylenediamine tetraacetic acid, H_4EDTA, except that it contains an asymmetric carbon atom and may be resolved. The optically active ligand will react with metal ions in a stereo-specific manner such that the rotation of the complex is different from that of the free base. If equivalent amounts of the metal complex containing one optical form of the ligand and the free optical antipode are mixed, the rate of loss of optical activity measures directly the rate of ligand exchange.

$$[M\textit{d}\text{-PDTA}] + \textit{l}\text{-PDTA} \rightleftharpoons [M\textit{l}\text{-PDTA}] + \text{d-PDTA} \quad (8)$$

The final value of the optical rotation will be zero corresponding to a random distribution. Table 2 shows the approximate times to reach zero rotation for a number of metal ions (*3*).

The rate of exchange is clearly a function of pH, being much faster in acidic solutions. This means that adding protons to $PDTA^{4-}$ to reduce its net charge, makes it a weaker complexing agent as Table 1 predicts. Preliminary studies (*3*) indicate that at *p*H 6 the reaction rate is first order in both the metal complex and the free ligand. For a polydentate ligand the mechanism is particularly difficult to unravel (*4*) so, leaving the details of how the reaction occurs unsettled, let us simply use Table 2 to compare different metal ions. The generally slower rates of exchange of

Table 2. Exchange of [M PDTA] in Water at 20°C (3)

Complex	*p*H	Time for zero rotation
Ca H_2PDTA	7.30	<1 min.
Mn H_2PDTA	3.00	<1 min.
	6.30	5 min.
Co H_2PDTA	2.90	<1 min.
	6.30	7 days
Ni H_2PDTA	0.70	30 min.
	2.90; 6.40	No exchange in 3 days
Cu H_2PDTA	2.90	<1 min.
	6.40	16 hours
Zn H_2PDTA	2.90	<1 min.
	6.32	3 hours
Cd H_2PDTA	2.90	<1 min.
	6.30	1 hour
Al HPDTA	2.90	20 hours
Y HPDTA	2.90	<1 min.
Fe HPDTA	0.7	7 hours
	6.5	No exchange in 2 days

the trivalent metal ions compared to the divalent metal ions are as expected, but nickel ion seems less labile than any of the trivalent ions despite its lower charge. The relative ion sizes are $Al^{3+} < Fe^{3+} < Y^{3+}$ which agrees with the observation that the last is the most labile.

The divalent cations fall into the order of decreasing lability $Ca^{2+} > Mn^{2+} > Cd^{2+} > Zn^{2+} > Cu^{2+} > Co^{2+} > Ni^{2+}$. The first three ions have ionic radii substantially larger than the last four and should be more labile, though cadmium which has the largest ion size is out of order with respect to rate. The variations in rate of the ions from zinc to nickel cannot be explained in terms of ion size since the sizes are all similar with copper(II) the smallest. We may also note that using H_4EDTA as the reference ligand, iron(II) is similar to cadmium(II) and zinc(II) in lability and cobalt(III) and chromium(III) are extremely inert (*5*).

Most substitution reactions of the divalent metal ions are very fast and special methods must be used to follow them. A very interesting example is supplied by solvent exchange studies done by means of nuclear magnetic resonance methods. It has been known for some time that paramagnetic ions will broaden the resonance signals observed in NMR spectra. Recently it has been shown that the changes enable rate constants for exchange reactions of the following kind to be measured (*6*):

$$[Cu(H_2{}^*O)_6]^{2+} + H_2O \rightleftharpoons [Cu(H_2O)_6]^{2+} + H_2{}^*O \quad (9)$$

The star is used simply to indicate a molecule of solvent originally coordinated to a metal ion to distinguish it from bulk solvent molecules. To get rate constants, one essentially uses the Heisenberg uncertainty principle expressed in the form $\Delta E \times \Delta t = h$. Here ΔE is the uncertainty in the energy as measured

by the broadness of the resonance line, Δt is the uncertainty in the life time of the excited state, and h is Planck's constant. The life-time in the case of a system not undergoing exchange would be T_B, the mean life of a given magnetic spin state for the nucleus. In an exchanging system the life-time may be τ_B, the mean time that a water molecule is coordinated to the metal ion. Whichever time is longer of T_B or τ_B will correspond to the rate determining step, so to speak, and will be the quantity measured. The reciprocal of τ_B is the first order rate constant for the forward step of reaction (9).

Table 3 presents some exchange data obtained in water and in methanol solutions of some paramagnetic ions by NMR. In most cases only lower limits can be put on the rate constants because of the possibility that T_B is rate controlling. Even so the data are tremendously valuable in that for the first time it is possible to get some idea of the permanence of a solvent molecule bound to the simpler ions. For some cases, such as Cu(II) and Ni(II) in methanol, it is clear that the rate of solvent exchange is being measured since the rates are the same for the methyl protons and for the hydroxyl protons. This would not be true if T_B were being measured.

Table 3. Lower Limits to Exchange Rate Constants, $1/\tau_B$, for Paramagnetic Ions in Water and Methanol at 25°C

Ion	$CH_3\underline{O}H$[a]	$\underline{C}H_3OH$[a]	$H_2\underline{O}$[b]
Cr^{3+}	2.1×10^4	7.0×10^3	10^{-6}[c]
Fe^{3+}	3.2×10^4	2.2×10^4	1.0×10^{4}[d]
Gd^{3+}	1.2×10^5	2.1×10^4	...
Mn^{2+}	2.5×10^5	1.8×10^4	2.2×10^7
Co^{2+}	1.1×10^4	1.7×10^3	3.1×10^5
Ni^{2+}	2.6×10^3	2.2×10^3	3.2×10^4
Cu^{2+}	1.0×10^4	1.0×10^4	3.3×10^5

All rate constants in sec^{-1}. The underlined atoms are the nuclei whose exchange rate (or rate of relaxation) is being studied.

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[c] HUNT, J. P., AND TAUBE, H., *J. Chem. Phys.*, **19**, 602 (1951).

[d] TAUBE, H., private communication.

It is of considerable interest that methyl alcohol molecules are exchanged more slowly than water molecules. This is either because they are held more firmly or because the methyl group offers steric hindrance to an incoming solvent molecule in an S_N2-like process. The very high lability of solvent attached to Fe(III) is noteworthy. The results are probably complicated by the fact that, even in the one molar acid solutions where the NMR spectra were taken, some $[Fe(H_2O)_5OH]^{2+}$ will exist and it is known that the hydroxy group is usually strongly labilizing for substitution reactions (*7*). Even so the water exchange rate constant is clearly very much greater than for an ion such as $[Cr(H_2O)_6]^{3+}$ where τ_B is about 10^6 seconds instead of 10^{-4}.

Table 4 presents some data on the sulfation reaction obtained by Eigen (*8*) using ultrasonic relaxation spectroscopy. It is strongly indicated by the rather complicated results that the process of forming a sulfato complex from an aquo complex consists of several stages. The first stages are concerned with the

Table 4. Rate Constants of Reaction (11) (Ref. 8)

$$[M(H_2O)_n]^{2+}, A^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M(H_2O)_{n-1}A] + H_2O \text{ at } 25° \text{ C.}$$

M	A	k_1, $sec.^{-1}$	k_2, $sec.^{-1}$
Be^{2+}	SO_4^{2-}	1×10^2	1.3×10^3
Mg^{2+}	SO_4^{2-}	1×10^5	8×10^5
Ca^{2+}	SO_4^{2-}	(10^7)[a]	(10^8)[a]
Mg^{2+}	$S_2O_3^{2-}$	1×10^5	1.5×10^6
Mg^{2+}	CrO_4^{2-}	1×10^5	1.5×10^6
Mn^{2+}	SO_4^{2-}	4×10^6	2×10^7
Co^{2+}	SO_4^{2-}	2×10^5	2.5×10^6
Cu^{2+}	SO_4^{2-}	(10^6)[a]	1×10^6
Ni^{2+}	SO_4^{2-}	1×10^4	1×10^5
Zn^{2+}	SO_4^{2-}	1×10^{8}[b]	1×10^{7}[b]

[a] The numbers in parentheses are relatively uncertain.

[b] EIGEN, M., private communication.

diffusion-controlled formation of an ion-pair or outer sphere complex.

$$[M(H_2O)_6]^{2+} + SO_4^{2-} \rightleftharpoons [M(H_2O)_6]^{2+}, SO_4^{2-} \qquad (10)$$

The last stage, and the one of chemical interest, is the rearrangement of this ion-pair to the true complex

$$[M(H_2O)_6]^{2+}, SO_4^{2-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [M(H_2O)_5SO_4] + H_2O \qquad (11)$$

Table 4 shows values of k_1 and k_2 for a number of metal ions. Some data for anions other than sulfate are also given.

The results show the expected dependence on electrostatic factors since small cations react more slowly than similar but larger ions. The transition metal ions show the order Mn(II) > Co(II) > Ni(II) < Cu(II) < Zn(II). Two other features are especially noteworthy: one is that the rate constant k_1 is apparently independent of the anion associated with the cation and the other is that the value of k_1 is remarkably similar to the rate constants for water exchange given in Table 3. This seems to be very powerful evidence for an S_N1 or dissociation mechanism operating in all these cases so that the rate step is the loss of a water molecule from the first coordination shell of the cation. Apparently the anion gives very little assistance in pushing off the leaving group.

Application of Crystal Field Theory

In order to make further sense out of the data given in the various tables it is necessary to correct the simple electrostatic theory by means of crystal field theory. As explained in reference *1*, this theory has to do chiefly with the splitting in energy of the *d* orbitals of a central metal ion produced by the electrostatic field (crystal field) of the attached ligands. The most important result, for present purposes, is to show that the electrons of a central atom with an incomplete *d* shell are not spherically distributed about the central atom. Instead the electrons will preferentially occupy the orbitals which lie furthest away from the ligands. This will lead to an increased stabilization of the complex ion over and above what a simple model based on spherical charge distributions would predict. This stabilization may conveniently be called *crystal field stabilization energy* (CFSE).

The great advantage of the crystal field theory is that many properties can be correlated and quantitative

predictions can be made. For example, the CFSE can be calculated from measurements of the energy splittings obtained from the visible absorption spectra of complexes.

Figure 1 shows the theoretical d orbital splittings for regular complexes of various geometries. For a filled d shell all orbitals will be occupied equally and there will be no stabilization. The electron distribution will be spherically symmetrical. For incomplete shells of electrons the more stable orbitals will tend to

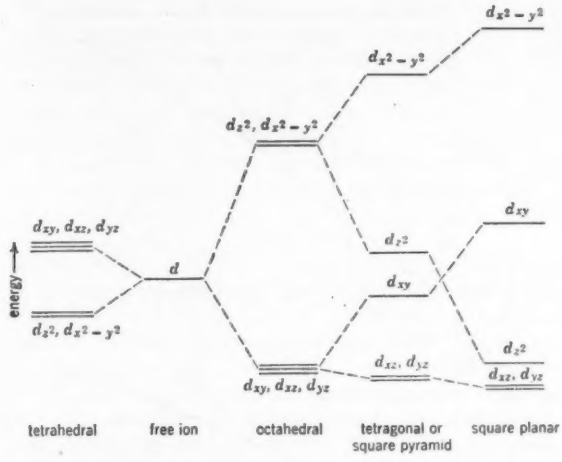


Figure 1. Crystal field splittings of the d orbitals of a central ion in regular complexes of different structures.

fill, giving rise to CFSE. The energy required to pair electrons in a single orbital must also be taken into account. A balance between this pairing energy and the energy differences between various orbitals will determine the electron distribution and, incidentally, the magnetic properties of the complex.

From spectral data the energy difference (known as $10Dq$) between the lower set of orbitals and the upper set in a regular octahedral complex can be found for various ligands. The order of smaller energy differences (weaker crystal fields) is $CN^- >$ 1,10-phenanthroline $> NO_2^- >$ ethylenediamine $> NH_3 > SCN^- > H_2O > F^- > RCO_2^- > OH^- > Cl^- > Br^-$. This order shows that electrostatic influence alone cannot account for the crystal field splittings. The other major factor is π-bonding (double bonding), both of the metal-to-ligand and of the ligand-to-metal type. Systems in which strong π-bonding occurs will not be adequately represented by an electrostatic model. Another complication will be covalent character in the σ-bond (single bond). However in most cases this seems to be smaller than has generally been assumed. The metal carbonyls and the organometallics will be exceptions.

For kinetic purposes we can easily see that a strongly crystal-field-stabilized system may be sluggish in its reactions. This is because in forming the transition state, by any mechanism, it is highly likely that a fair amount of CFSE will be lost. This effect is very large for octahedral complexes in the case of d^3, spin coupled d^6 and spin-free d^8 systems. As an example Table 5 gives the theoretical predictions and the experimental results for the dissociation of a series of phenanthroline and dipyridyl complexes of metal ions of the first transition series. It is assumed that an S_N1 mechanism is operating and that something resembling a square pyramid, five-coordinated intermediate is formed.

The procedure is then to use the energy levels such as are shown in Figure 1 to calculate the CFSE in the original complex and in this five-coordinated intermediate (the energy levels are the same for a square pyramid containing five groups as for a tetragonal structure with four groups close to the metal ion and two groups further away). For example, for nickel(II) an octahedral complex has $12Dq$ units of crystal field stabilization (*1*). A square pyramid has $10Dq$ units of CFSE, taking the numerical values of the energy levels upon which Figure 1 is based (*9*). Accordingly there is a loss of $2Dq$ units of energy in going from the reactant to the intermediate. It may be assumed that this represents an increment to the necessary activation energy for reaction. Of course other changes in energy occur on reaction and the total activation energy will be much higher than $2Dq$. For example, a metal-to-nitrogen bond must be broken, quite independent of the electronic structure of the metal ion.

Table 5 gives the experimental rate constant and the experimental activation energy where known. The statement "fast" is used for those cases where the complex reacts too rapidly to study by ordinary means.

Table 5. Kinetic Data and Crystal Field Stabilization Energy Changes for the Dissociation of Bivalent Metal Complexes of Phenanthroline and Dipyridyl at 25° (26)

Electronic system	$\Delta E(Dq)$	Complex ion	k_{diss} (min.$^{-1}$)	E_{act} (kcal mole^{-1})
d^3	2	$V(phen)_3^{2+}$	Slow ?	...
d^5	0	$Mn(dipy)_3^{2+}$	Fast	...
d^6	4	$Fe(phen)_3^{2+}$	0.0043	32.1
		$Fe(dipy)_3^{2+}$	0.0089	28.4
d^7	0	$Co(phen)_3^{2+}$	12.66	20.6
		$Co(dipy)_3^{2+}$	Fast	...
d^8	2	$Ni(phen)_3^{2+}$	0.005	25.2
		$Ni(phen)_3^{2+}$	0.0011	23.1
		$Ni(phen)^{2+}$	0.0095	26.2
		$Ni(dipy)_3^{2+}$	0.137	22.4
d^9	0	$Cu(phen)_3^{2+}$	Fast	...
d^{10}	0	$Zn(phen)_3^{2+}$	Fast	...

Since the spectral value of Dq for phenanthroline and dipyridyl is about 4 kcal, it is seen that there is very good agreement between the theory and the experimental observations. Thus there should be a contribution of $4Dq$ to the activation energy for iron(II) and no crystal field activation energy for cobalt(II). The difference in activation energies of 11 kcal should then equal $4Dq$. Because of the assumption as to the transition state and because other factors can influence the rates somewhat, perfect agreement cannot be expected. The slow reaction of iron(II) is predicted only for diamagnetic complexes (spin coupled). The slowness of reactions of Ni(II) compared to Mn(II), Co(II), Zn(II), and Cu(II) is nicely accounted for by the theoretical considerations. It should be noted that the discrimination in rates depends on the crystal field strength of the ligand and will be less for water, etc., than for phenanthroline.

Role of Effective Ionic Charge

At this point it is desirable to explain another correction to the simple electrostatic theory. This is a necessary correction because it turns out that the combined effects of charge, size, and ligand field theory are not enough to account for the differences in behavior of all metal ions. Thus gold(I), even though larger in size than potassium ion, forms more stable complexes and its heat of hydration and ionization potential are greater. The explanation for all of these phenomena seems to be tied up with a single obvious extension of the electrostatic theory. This is the concept of the "effective ionic charge" as opposed to the nominal charge (*10*). It is well known classically that for spherical distributions of negative charge, such as the electron clouds surrounding an ion with filled electron shells, the negative potential acting on a test charge located *within* the charge distribution is not given by q/r but is less than this. Here q is the total amount of negative charge and r is the distance of the test charge from the center of the distribution. This means that a test charge located well within the electron cloud of a cation will be subject to a positive potential q'/r where the effective charge, q', is somewhat greater than the nuclear charge minus the number of electrons.

In other words, electrons far removed from the nucleus do not completely screen the positive charge of the nucleus. Particularly d electrons, which project far out, are inefficient in screening the nucleus and it is just those ions with a large number of d electrons which display the properties to be expected for an effective charge some 10–20% greater than the nominal positive charge. This is particularly true for the third transition series.[2]

A negative charge whether it be an electron or a ligand will be held more firmly by such an ion than by an ion with an inert gas electronic structure of the same nominal charge and crystallographic radius. There is in fact a remarkable linear correlation between total ionization potentials to form metal ions and their heats of hydration (*11*) which indicates a common effect. Since electrostatic energies control ionization potentials, it seems reasonable to assume that the heat of hydration, the greater part of which is due to coordination of the first layer of water molecules, is also principally determined by electrostatic forces.

Figure 2 shows the heats of hydration of the divalent and trivalent ions of the first transition series plotted against atomic number. The reaction involved is, for example,

$$Ni^{2+}(g) \rightarrow Ni(H_2O)_6^{2+}(aq) \qquad (12)$$

the heat of reaction (12) being calculated from a thermochemical cycle. The black circles are the calculated heats from experimental data and the unfilled circles are the heats corrected for CFSE as first suggested by Orgel (*12*). The heats of hydration thus corrected lie on or near a line rising smoothly from calcium to zinc, or scandium to gallium. The rise is due to the effective ionic charge increasing steadily with the number of d electrons.

The combined influences of effective charge, ion size, and crystal field stabilization then determine the properties of the complexes of the metal ions. The three factors together form a unified electrostatic theory which is extremely useful. It must be remembered, however, that it does represent only an approximation to the more complicated situation actually existing in the molecule or complex ion.

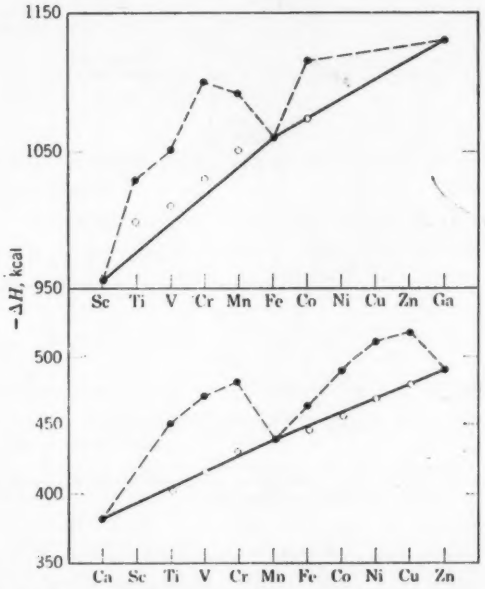


Figure 2. Heats of hydration of the divalent (lower) and trivalent (upper) ions of the first transition series. Dotted line is for uncorrected and solid line for crystal field corrected values.

Substitution Reactions of Octahedral Complexes

The well studied examples of cobalt(III), a d^6 system, and chromium(III), a d^3 system, provide much of the available data on substitution reactions of octahedral complexes. The slowness of these reactions, e.g., the acid hydrolysis or aquation reaction,

$$Co(NH_3)_5Cl^{2+} + H_2O \rightarrow Co(NH_3)_5H_2O^{3+} + Cl^- \qquad (13)$$

is a consequence of the small size and high charge of the metal ion on the one hand and very large ligand field effects on the other. The same factors enter into the even slower reactions of the analogous d^6 compounds $Rh(NH_3)_5Cl^{2+}$ and $Ir(NH_3)_5Cl^{2+}$. Since the Rh^{3+} and Ir^{3+} ions are larger than Co^{3+}, it would be difficult to account for the greater difficulty of hydrolysis if it were not for the corrections to the simple electrostatic theory. However the second and third transition series ions have higher effective charges than cobalt and larger crystal field effects. Thus it is known from spectral data that Dq for iridium is almost twice as large as for cobalt (*13*).

Let us consider further some of the kinetic consequences of the d orbital electrons in these examples. The six d electrons fill up the octahedral faces with a cloud of charge extending well out from the central atom. They represent a formidable barrier to an S_N2 attack by an electron-donating, or nucleophilic,

[2] These properties of ions with non-inert gas electron structures were first recognized by Fajans who correctly correlated them with the large polarizabilities of these same ions. [FAJANS, K., *Naturwissenschaften*, 11, 165 (1923).]

reagent since it is just these open faces that might be considered the logical points of entry for such reagents. Furthermore the energy levels of Figure 1 can help us predict something about the geometry and coordination number of probable transition states or intermediates. For example, an incoming reagent in earlier days was often thought of as attacking at an octahedral edge and forming a transition state with five groups in a plane and two groups above and below this plane. This would be a pentagonal bipyramid. The energy levels of such a system when filled with six electrons give a CFSE of $15.5Dq$ as compared to $24Dq$ in the original complex. This represents a loss of $8.5Dq$ which would contribute to the activation energy. The energy loss is so large as to make this particular reaction route impractical.

If an S_N1 mechanism operates there are two probable geometries for the intermediate of coordination number five that would be formed, the square pyramid and the trigonal bipyramid both of which are illustrated in Figure 3. It can again be calculated that the energy levels of the trigonal bipyramid are not favorable for six d electrons. Only in the special case that one of the remaining five ligands is an electron donating group (π-bonding) does such a rearrangement become plausible since strong π-bonding to the metal is possible only in the trigonal form.[3] The removal of one group, leaving the others undisturbed, produces the least perturbation of the electronic energy levels and the least loss of CFSE. This would be the square pyramid intermediate. If the chloride ion is removed from $Co(NH_3)_5Cl^{2+}$ to form $Co(NH_3)_5^{3+}$, for example, it is very unlikely that this species could survive even a few molecular collisions with such a vacant position in its coordination shell. Instead the first available molecule or ion that can act as a ligand will fill up the vacant spot. In fact, using thermochemical data and the electrostatic model as a basis for calculation (*14*) it is easy to show that it is not possible to form $Co(NH_3)_5^{3+}$ in any geometry without an excessive expenditure of energy. That is, the coordinate bond energy,

$$Co(NH_3)_5Cl^{2+} \rightarrow Co(NH_3)_5^{3+} + Cl^- \quad \therefore \quad (14)$$

is simply too large, about 94 kcal per mole in solution for a square pyramid structure.

Since the experimental activation energy for the acid hydrolysis reaction is only 24 kcal, it is necessary to find a lower energy reaction path. This creates a visualization of the mechanism of reaction of such an ion as one in which the Co—Cl bond is lengthened to some critical distance, at which point a solvent molecule slips in to occupy the place of the chloride ion, which is then completely expelled. The assignment of an S_N1 label or an S_N2 label to such a process is somewhat ambiguous.

It may be stated that the bulk of the experimental evidence on cobalt(III) and chromium(III) complexes favors an S_N1 mechanism. Referring to Table 1, it is found that the effect of changing the charges and sizes of the labile ligand and the inert ligands and the effect of the external reagent is generally that predicted for an S_N1 mechanism. For example, in water solution it is not possible to find a reagent which appreciably accelerates the release of a labile group. An exception is hydroxide ion for which a special mechanism appears to operate (see below). It is extremely difficult to find any external reagent which will directly replace the chloride ion. This is because the ubiquitous

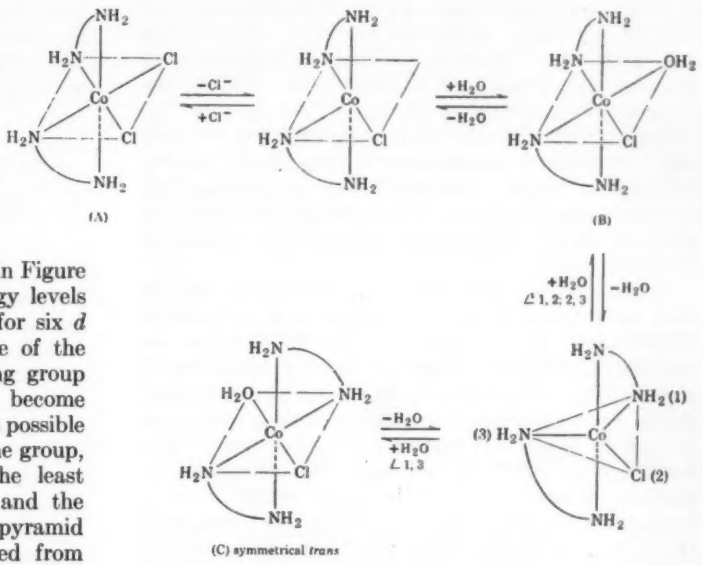


Figure 3. Square pyramid and trigonal bipyramid intermediates in the S_N1 reactions of an octahedral complex. The reactions shown are for the racemization of optically active *l-cis*-$Co(en)_2Cl_2^+$ by way of inactive *trans*-$Co(en)_2(H_2O)Cl^{2+}$.

solvent always seems to react first. Eventually, of course, a substitution reaction in which the coordinated solvent dissociates and an adjacent reagent ion takes its place will occur (the anation reaction).

In the case of a non-aqueous solvent, or, more specifically a non-coordinating solvent, it should be possible to find examples of nucleophilic reagents which increase the rate of release of the labile group. In the case of an anion, this will probably involve formation of an ion-pair first. The anion will then be in a position to slip into the coordination sphere as the bond to the leaving group lengthens. In such a system the decision to call the mechanism an S_N2 process or an S_N1 process (dissociation of the ion-pair) will depend on whether the reaction rate is greatly influenced by the nucleophilic character of the anion.[4]

It may also be argued that in an octahedral system, the number of groups surrounding the central atom will predispose the complex to react by a dissociation mechanism. That is, the ion becomes too crowded if seven ligands are brought close together. This factor

[3] The repulsion between the five ligands is less in a trigonal bipyramid than in a square pyramid. However, ligand field effects usually overshadow this.

[4] Adamson, A. W., *J. Am. Chem. Soc.*, **80**, 3183 (1958), calls all of the above mechanisms for octahedral complexes S_N2FS. The FS, meaning front-side, emphasizes that the entering group will come in on the same side as the leaving group. This leads to retention of configuration.

is due to the mutual repulsion of the ligands by both van der Waals' and electrostatic forces and is independent of the existence, or non-existence, of outer *d*-orbital electrons. In this connection it would be extremely valuable to have rate studies of the substitution reactions of octahedral complexes where there are no *d*-orbital electrons, or where the *d* electrons are well buried. Such systems would be SiF_6^{2-}, AsF_6^-, and the like.[5]

It would of course be presumptuous to believe that a single mechanism operates for all substitution reactions of octahedral complexes. Table 1 predicts that increasing the charge on the central atom will favor an S_N2 mechanism. There is no clear-cut evidence that this expectation has been fulfilled. For example, the octahedral complexes of platinum(IV), such as $Pt(NH_3)_5Cl^{3+}$, do not react with nucleophiles in a simple way.[6] Instead a roundabout mechanism is usually followed in which some reduction to platinum(II) occurs and then a reaction of the platinum(IV) complex with the nucleophilic reagent catalyzed by platinum(II) (*15*).

In the case of cobalt(III) it is easy to see that an inert substituent X in a compound such as $Co(en)_2XCl^{2+}$ might play a dominant role in deciding the reaction mechanism. Thus an electron donating X such as NH_2, OH or Cl would favor an S_N1 mechanism, chiefly by π-bonding (*16*), and an electron attracting X such as NO_2 would favor an S_N2 mechanism. The latter group would operate both by increasing the positive charge on the cobalt atoms, which favors a displacement mechanism, and also by partly removing the *d* electrons on the cobalt which provide a powerful hindrance to the approach of an incoming reagent.

A Reactivity Order for Nucleophiles?

Considering the displacement reactions of organic chemistry, various nucleophilic reagents can be arranged in an order of increasing reactivity (*17*). This order naturally varies somewhat with the nature of the electrophilic substrate, but one can generally expect that hydroxide ion, for example, will be a good reagent and nitrate ion will be a poor reagent. It is of interest to see if an order of nucleophilic reactivity exists toward metal ions and if it is about the same as for carbon. In particular what effect do the *d* electrons of a metal ion have on the rates of reaction of various possible nucleophilic ligands?

Octahedral Complexes

As mentioned earlier, it is not easy to get such information for octahedral complexes because S_N2 reactions for these systems are certainly not common. There is the special case of the hydroxide ion which does react very rapidly with many complexes. The reaction is called base hydrolysis.

$$Co(NH_3)_5Cl^{2+} + OH^- \rightarrow Co(NH_3)_5OH^{2+} + Cl^- \quad (15)$$

Again most of the kinetic studies to date have been done on cobalt(III) complexes. For ammine complexes containing N—H bonds, the rate of base hydrolysis is often as much as a million times faster than the corresponding rate of acid hydrolysis. It has long been known that the rate of base hydrolysis is second-order, being first-order in complex and first-order in hydroxide ion. One interpretation is that the reaction is S_N2 involving a nucleophilic displacement by hydroxide ion on cobalt(III). A second interpretation is credited to F. J. Garrick who suggested a pre-acid-base equilibrium followed by a rapid rate determining dissociation of the conjugate base (S_N1CB mechanism). This sequence is also consistent with the observed second-order kinetics.

$$[Co(NH_3)_5Cl]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2Cl]^+ + H_2O \quad (16)$$

$$[Co(NH_3)_4NH_2Cl]^+ \overset{\text{slow}}{\rightarrow} [Co(NH_3)_4NH_2]^{2+} + Cl^- \quad (17)$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \overset{\text{fast}}{\rightarrow} [Co(NH_3)_5OH]^{2+} \quad (18)$$

There has been considerable speculation as to whether the base hydrolysis of cobalt(III) ammines proceeds by an S_N2 or an S_N1CB mechanism. The mechanisms are sufficiently different so that, in principle, it is possible to distinguish between them. For example clearly the S_N1CB mechanism requires an acidic proton in the complex. The facts are that complexes containing no acidic protons do not react rapidly with hydroxide ion as a rule; although, depending on the nature of the complex, certain reactions can be accelerated by the presence of base. In the area of hydrolysis reactions, it is striking that the rate of release of nitrite ion in the case of *trans*-dinitro-bis(2-2′-bipyridine)cobalt(III) and the release of chloride ion in the case of *trans*-dichloro-(P,P,P′,P′ tetraethyl ethylene diphosphine) cobalt(III) is independent of hydroxide ion concentration even at *p*H's of 11 to 12. The most convincing evidence for the S_N1CB mechanism is the recent demonstration of the existence of the 5-coordinated intermediate of reaction (*18*).

Both of the possible mechanisms give rise to the same hydroxo product in water because water is a good coordinating agent and because a proton shift is very fast. However in a non-hydroxylic solvent different products are predicted for the two mechanisms in the event that an excess of some nucleophilic reagent other than hydroxide ion or water is present. The results of recent studies using dimethylsulfoxide as a solvent are readily explained by the S_N1CB mechanism but cannot be explained by the S_N2 mechanism (*18*). For example it was observed that reactions of the type

$$[Co(en)_2ACl] + NO_2^- \rightarrow [Co(en)_2ANO_2] + Cl^- \quad (19)$$

are slow (half-life of hours) but in the presence of catalytic amounts of hydroxide ion the reaction is very fast (half-life of only a few minutes) and the product continues to be $[Co(en)_2ANO_2]$. Further, the reaction between $[Co(en)_2AOH]$ and NO_2^- is slow; this rules out a rapid S_N2 displacement path followed by a rapid reaction with nitrite ion. Instead, the results support the formation of an active 5-coordinated intermediate which then reacts rapidly with NO_2^-.

[5] In this connection it is interesting to note that AsF_6^- is stable to strong base even on boiling and evaporation to near dryness. On the other hand, AsF_5OH^- is fairly easily hydrolyzed. [Dess, H. M., and Parry, R. W., *J. Am. Chem. Soc.*, **79**, 1589 (1957).]

[6] It is possible that the reaction between $PtCl_6^{2-}$ and I^- is a simple S_N2 process. [Poë, A. J., and Vaidya, M. S., *Proc. Chem. Soc.*, 118 (1960).]

This mechanism receives further support from the observation that the rate of formation of $[Co(en)_2AY]$ depends only on the concentration of base and not on the nature or concentration of Y. Hydroxide ion and piperidine were used as catalysts, while nitrite, thiocyanate, and azide ions were used as nucleophilic reagents Y. Under the same condition all three nucleophiles reacted at the same rate. It is clear that although these results cannot be explained by an S_N2 process, they are readily accounted for by the S_N1CB mechanism.

$$[Co(en)_2ACl] + B \overset{\text{fast}}{\rightleftharpoons} [Co(en)(en\text{-}H)ACl] + HB^+ \quad (20)$$

$$[Co(en)(en\text{-}H)ACl] \overset{\text{slow}}{\rightarrow} [Co(en)(en\text{-}H)A] + Cl^- \quad (21)$$

$$[Co(en)(en\text{-}H)A] + NO_2^- \overset{\text{fast}}{\rightarrow} [Co(en)(en\text{-}H)ANO_2] \quad (22)$$

$$[Co(en)(en\text{-}H)ANO_2] + BH^+ \rightarrow [Co(en)_2ANO_2] + B \quad (23)$$

Square Planar Complexes

Thus it is not now possible to set up a scale of nucleophilic reactivities using octahedral complexes. However, turning to the square planar complexes of coordination number four, the prediction may be made that S_N2 mechanisms are much more probable than they are for octahedral systems because of the "vacant" positions above and below the square plane. Energetically speaking, it is quite improbable that these positions are truly vacant. Instead solvent molecules, or other molecules or ions, will certainly be in these positions as a great deal of evidence now shows. In the electrostatic theory square complexes exist only because of strong crystal field effects, since otherwise four ligands around a central atom would arrange themselves tetrahedrally to minimize ligand repulsions. But the crystal field influence of a ligand falls off very rapidly with distance, so that it is possible to have four groups close in and two groups further away, a tetragonal arrangement, and still have essentially the CFSE of a square planar complex.

The groups above and below the plane will be labile, however, and may easily be replaced by various reagents in solution. This sets the stage for the displacement of the most labile group in the plane of the complex. The incoming reagent is in a position to help force it out. Various possibilities exist for the detailed process whereby the labile ligand leaves and the entering group appears in the plane. In discussing these it is necessary to bear in mind the electron distribution. In the typical case of nickel(II), or platinum(II), all d orbitals are filled except the $d_{x^2-y^2}$ which lies in the plane of the complex. Hence electrons project above and below the plane.

There are two possible mechanisms for which some evidence exists. In the first, a square pyramid is formed as an intermediate. This could happen by the groups above and below the plane moving in closer to the metal atom, simultaneously displacing the most labile group in the plane. The intermediate could react either with Y directly or with solvent. In the latter case, the solvent is usually not held very strongly and would be quickly replaced by Y.

Figure 4 shows the details of another possible mechanism in which a trigonal bipyramid is formed as an intermediate. In this case there is a direct displacement of X by Y. Of course the solvent may also act as a nucleophilic reagent in some cases. Again, there is a greater loss of CFSE in forming a trigonal bipyramid than a square pyramid intermediate. If strong π-bonding groups are present in the complex, then the trigonal bipyramid becomes the more probable form.

There is an interesting difference between the planar and octahedral complexes, however. From Figure 1 it can be seen that the characteristic of a planar complex is that one d orbital is very high in energy. Hence the systems that form such complexes will be those with the right number of d electrons to leave this orbital empty, or at least half-empty. These will be d^4, d^5 (spin-paired) and d^9 systems. Hence there are extra electrons in these complexes compared to the octahedral cases of d^3, d^6 (spin-paired) and d^8 (spin-free). The ligands that promote formation of a trigonal bipyramid intermediate in the planar case must therefore be groups that can *accept* electrons from the metal atom such as PR_3, CO and NO_2^-. In the octahedral systems the ligands that favored a trigonal form were electron donators to the metal, such as OH^- and Cl^-.

It is found experimentally that a number of reagents can influence the rate of reaction of planar complexes of platinum(II) and palladium(II)

$$PtA_2LX + Y \rightarrow PtA_2LY + X \quad (24)$$

The rate law is given by the general expression (*19*)

$$\text{Rate} = k_1[\text{Complex}] + k_2[Y][\text{Complex}] \quad (25)$$

where k_2 is a second-order rate constant for an S_N2 mechanism involving Y as a nucleophilic reagent. The term k_1 is a first order constant which is interpreted also as an S_N2 reaction in which the solvent is the reagent. The reason for this is that structural changes in PtA_2LX cause k_1 and k_2 to change in the same direction. For example, large, bulky groups A or L cause k_1 and k_2 to decrease very markedly because of steric hindrance to the close approach of the nucleophilic reagent. Either the first or second term of equation (25) often predominates.

Using k_2 as a measure, it is possible to list roughly a number of nucleophiles Y in order of decreasing

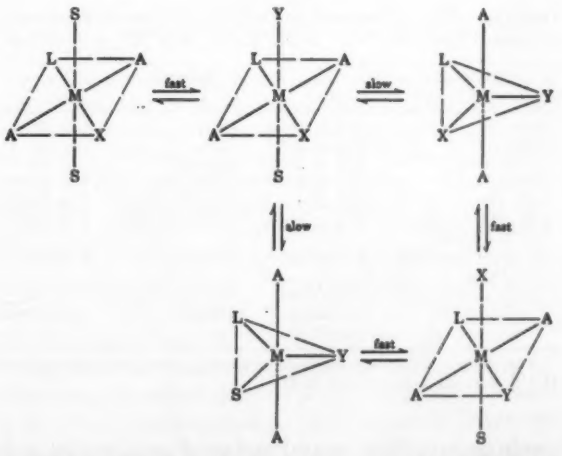


Figure 4. Substitution mechanism for square complex with trigonal bipyramid intermediate.

reactivity toward platinum(II) (*20*):

$$R_3P \sim \text{thiourea} \sim SCN^- \sim I^- > N_3^- > NO_2^- > \text{pyridine} > \text{aniline} > \text{olefin} \sim NH_3 \sim Br^- > Cl^- > \text{glycine} \sim OH^- \sim H_2O$$

The reactivity order varies somewhat with the exact platinum complex used, but the changes are small. This order may be compared with the order of reactivity of some of the same groups toward a typical organic substrate such as an alkyl halide (*17*):

$$\text{thiourea} > I^- > SCN^- > OH^- > NH_3 \sim \text{aniline} > NO_2^- > N_3^- > \text{pyridine} > Br^- > Cl^- > \text{acetate} > \text{olefin}$$

The orders are somewhat similar except for hydroxide ion and the olefinic double bond. The latter (as typified by allyl alcohol) is a very good ligand for platinum and reacts quite rapidly. For organic halides the double bond has very poor nucleophilic properties. It is well known that the bonding of olefins to platinum, as in Zeise's salt $Pt(C_2H_4)Cl_3^-$, is due to the presence of *d* electrons on the metal ion (*21*). Hydroxide ion, on the other hand, has a rather high reactivity for organic halides but no measurable reactivity toward platinum(II). It may be mentioned also that the hydroxide ion shows only a low order of reactivity toward the octahedral chloro complexes of platinum(IV) and of rhodium(III) (*22*). Even the small effects observed may be due to the S_N1CB mechanism postulated for cobalt(III) complexes.

Solvent Effects

An extensive study has been made of the effect of solvent on the rate of the isotope exchange experiment (*23*)

$$\textit{trans}\text{-Pt(pyridine)}_2Cl_2 + 2{}^*Cl^- \rightleftharpoons \textit{trans}\text{-Pt(pyridine)}_2{}^*Cl_2 + 2Cl^- \quad (26)$$

The symbol *Cl is used to designate the radioactive isotope ^{36}Cl. Some of the results obtained are listed in Table 6. The solvents studied fell into two categories: (A) those where the rate of chloride exchange does not depend on the chloride ion concentration, $k_1 \gg k_2$ $[Cl^-]$ in equation (25); and (B) those solvents where the rate is first order in free chloride ion concentration, $k_2\,[Cl^-] \gg k_1$. Poor coordinating or ionizing solvents are in group (B) in general and good coordinating and ionizing solvents are in group (A). We can then call the group (A) solvents good nucleophiles to platinum(II) compared to those of group (B), though sometimes there are special reasons why some of the (B) solvent molecules are not effective in displacing chloride ion from the complex.

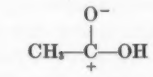
Table 6. Effect of Solvent on the Rate of Chloride Exchange in *trans*-$[Pt(py)_2Cl_2]$ $^{36}Cl^-$ at 25°C and $[R_4N^{36}Cl] = 0.001$ M

Solvent (A)	k_{obs}, min.$^{-1}$	Solvent (B)	k_{obs}, min.$^{-1}$
H_2O	2.1×10^{-3}	CCl_4	1×10^{-4}
C_2H_5OH	8.5×10^{-4}	C_6H_6	2×10^{-4}
n-C_3H_7OH	2.5×10^{-4}	m-cresol	2×10^{-4}
$(CH_3)_2SO$	2.3×10^{-2}	t-C_4H_9OH	1×10^{-3}
CH_3NO_2	1.9×10^{-3}	CH_2ClCH_2Cl	7×10^{-4}
CH_3NO_2 (2.2M CH_3COOH)	2.4×10^{-2}	$CH_3COOC_2H_5$	4×10^{-5}
C_2H_5OH (0.075M H_3BO_3)	3.1×10^{-3}	$(CH_3)_2CO$	4×10^{-4}
Glacial acetic acid	(Too fast to measure)	$HCON(CH_3)_2$	9×10^{-4}
		CH_3CN	1×10^{-3}

For solvents (A) the rate of exchange does not depend on $[C]^-]$, but for solvents (B) it does.

Comparing the group (A) solvents in order of relative efficiency with their behavior toward solvolytic reactions of organic halides (*24*) we find again some correspondences and some discrepancies. For example, acetic acid and nitromethane are much better nucleophiles toward platinum than toward carbon. Also, there is no parallel in organic chemistry for the catalytic effect of boric acid. It may be mentioned that the boric acid and acetic acid molecules show a rate acceleration. Borate ion and acetate ion are ineffective.

Contemplating all the reagents and the solvents which show unexpectedly high reactivity toward platinum, a common feature can be distinguished. All of these ions or molecules have available either low energy empty orbitals or orbitals that can be readily vacated. For example, the electronic structure for acetic acid



is not very unstable and presents an empty *p* orbital on the carboxyl carbon. Even iodide ion falls into the above category since it has empty *d* orbitals which are low in energy (chloride ion has only higher-energy empty *d* orbitals). A possible explanation for the reactivity of these substances then, is that in the transition state for reaction, π-bonding occurs between the filled *d* orbitals of platinum and these empty *p* or *d* orbitals on the nucleophilic reagent. Figure 5 shows how such π-bonding may make it easier for a basic atom (needed for coordination) to approach the platinum atom closely.

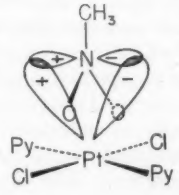


Figure 5. π-Bonding (metal to ligand) in the interaction of solvent molecules with platinum(II). Only the upper lobes of a *d*-orbital on platinum are shown.

Summary

Thus a good nucleophilic reagent for metals having excess *d* electrons is one that can both donate electrons to the metal ion and accept electrons from the metal ion. Such a molecule may be called a "biphilic" reagent (*20a*). The low efficiency of hydroxide ion as a nucleophilic reagent toward some of the higher transition metals may be explained by considering Figure 5 again. A nucleophile with all of its orbitals filled with electrons will experience considerable repulsion as it approaches the *d* orbitals of platinum. The repulsion is due to the operation of the Pauli exclusion principle and is more than just an electrostatic effect. One pair of electrons either on the metal or on the incoming ligand must be raised to a higher energy level because of the Pauli principle. A group such as carboxyl or nitro

can provide another electronic level easily, but hydroxide ion, fluoride ion, and ammonia can not.

To answer our original question, it appears true that the presence of outer *d* electrons in the central atom of a complex will affect the rate of reaction of various groups which can act as ligands. Compared to the carbon atom of organic chemistry, such metal atoms may show quite a different order of nucleophilic reactivities. Of course, for metal ions with no outer *d* electrons, such as titanium(IV) or tin(IV), it is expected that the correspondence to organic chemistry will be closer. Hydroxide ion may again function as a good nucleophilic reagent in such cases, as seems to be affirmed experimentally (*25*).

Acknowledgment

Thanks are due to the U.S. Atomic Energy Commission for support of much of the work described in this article.

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Herbert C. Brown
Purdue University
Lafayette, Indiana

New Selective Reducing Agents

The discovery of sodium borohydride in 1942 (*1*) and of lithium aluminum hydride in 1945 (*2*) brought about a revolutionary change in the procedures utilized for the reduction of functional groups in organic chemistry (*3*, *4*). Today, faced with the problem of reducing a carbonyl, ester, or nitrile group, the synthetic chemist will rarely undertake to use the Meerwein-Ponndorf-Verley reaction, the Bouveault-Blanc procedure, or catalytic hydrogenation. The complex hydrides provide such a simple convenient route for the reduction of such functional groups that they are invariably applied in laboratory syntheses involving such reductions.

In spite of their great convenience, these two reagents suffer from certain deficiencies. Thus, lithium aluminum hydride is an exceedingly powerful reducing agent, capable of reducing practically all of the functional groups utilized by the organic chemist. This great reactivity renders it relatively difficult to apply for selective reductions. On the other hand, sodium borohydride is a relatively mild reducing agent, one which reacts readily only with aldehydes, ketones, and acid chlorides. Consequently, it is useful only for selective reductions involving these reactive groups (*3*, *4*).

This situation made it desirable to develop means of controlling the reducing power of such reagents. It was evident that if such control could be achieved, either by decreasing the reducing power of lithium aluminum hydride or by increasing that of sodium borohydride, or

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Presented as part of the Symposium on Recent Advances in Inorganic Chemistry, sponsored jointly by the Divisions of Inorganic Chemistry and Chemical Education, at the 137th Meeting of the ACS, Cleveland, Ohio, April, 1960.

This work was made possible by Contracts DA-33-008-ORD-992 and 2002 supported by the Office of Ordnance Research, U. S. Army, and by grants provided by Parke, Davis and Company, the Upjohn Company, and the American Cyanamid Company. This assistance is gratefully acknowledged.

both, there would become available to the organic chemist a complete spectrum of reagents for selective reductions. With organic research undertaking the synthesis of structures of increasing complexity, there was an evident and growing need for reagents capable of a high degree of selectivity.

Four means of controlling the reducing power of the complex hydrides suggested themselves. First, it appeared that the reducing power might be influenced by the solvent. Second, the cation in the complex hydride might be expected to alter the reducing power. Third, substituents in the complex ion should exert marked steric and electronic influences upon the reactivity of the substituted complex ion. Finally, the development of acidic reducing agents, in contrast to the basic nature of the complex hydride salts, might be expected to alter greatly the relative reactivities of different groups toward reduction. Accordingly, several years ago we undertook a program of research to investigate these possibilities. The present discussion will summarize our progress toward these objectives.

Solvent Effects

Sodium borohydride has the great advantage over lithium aluminum hydride in that it may be utilized in a much wider range of solvents. Thus it is highly soluble in water, reacting only slowly with the solvent to evolve hydrogen. Even this slow reaction is markedly decreased by the addition of alkali (*1*), and stable solutions of sodium borohydride in strong caustic are commercially available. Such aqueous solvents readily reduce aldehydes and ketones, even in cases where the solubilities of the compounds in the aqueous system are quite limited.

$$4R_2CO + NaBH_4 \rightarrow Na[B(OCHR_2)_4]$$

$$\downarrow 4\,H_2O$$

$$NaB(OH)_4 + 4R_2CHOH$$

The reducing agent is readily soluble in methyl and ethyl alcohols (*1*). It reacts rapidly with methyl alcohol, but only slowly with ethyl alcohol. Thus 100% evolution of hydrogen is observed in methanol in 24 minutes at 60°, whereas under the same conditions in ethanol the evolution is less than 2%. It is unfortunate that early procedures emphasized the use of methanol as a solvent (*5*), so that it is still commonly applied, although ethanol possesses the obvious advantage of permitting reductions in homogeneous solution with relatively little loss of the reducing agent through this side reaction with the solvent.

Sodium borohydride possesses only a modest solubility (0.1 *M* at 25°) in isopropyl alcohol. However, this solvent possesses the great advantage of being quite stable toward the reagent—standard solutions of sodium borohydride in this solvent have exhibited no measurable change in active hydride over periods of several weeks. Consequently, this solvent not only is convenient for reductions on a preparative scale, but it made possible kinetic studies of the reduction of aldehydes and ketones (*7*, *8*).

The very great difference in reactivity between benzaldehyde and acetophenone observed in these kinetic studies is noteworthy. Thus the second order rate constant for acetophenone at 0° is 2.05×10^{-4} l.mole^{-1} sec^{-1}, whereas the corresponding constant for benzaldehyde is 820×10^{-4} l.mole^{-1} sec^{-1}. With a factor of 400 in rate constants, it is evident that aldehyde groups should readily be reduced selectively in the presence of related ketone groupings.

Sodium borohydride is insoluble in ethyl ether, only slightly soluble in tetrahydrofuran, but readily soluble in diglyme (dimethyl ether of diethylene glycol) and triglyme (dimethyl ether of triethylene glycol). The solubility of sodium borohydride in diglyme reaches a maximum (~3 *M*) in the neighborhood of 40°, with greatly reduced solubilities at 0° (0.3 *M*) and 100° (0.1 *M*). At 0° a 1:1 solvate with diglyme separates from the solution; at 100°, the unsolvated salt separates. Consequently, this medium is a convenient one for the preparation of sodium borohydride of high purity. In triglyme the solubility is high (~3 *M*) and does not vary greatly with temperature.

These solutions in diglyme and triglyme have proven very useful in utilizing sodium borohydride for the generation of diborane (*9*) and for the hydroboration of olefins (*10*, *11*). However, instead of enhancing the reducing power of sodium borohydride, these solvents appear to decrease it. No significant reduction of acetone was observed in diglyme solution under conditions where the ketone is quantitatively reduced in aqueous or alcohol solution in a matter of minutes (*6*).

Aldehydes are reduced by solutions of sodium borohydride in diglyme (*12*), so that such solutions may be effective for the selective reduction of aldehydes in the presence of ketones.

Although occasional references have appeared in the literature on the use of pyridine or acetonitrile as solvents for sodium borohydride reductions, no detailed study has been reported on the influence of these solvents on the reducing power of borohydride. However, in view of the greatly decreased reducing power of diglyme solutions as compared to solutions of borohydrides in hydroxylic solvents, it is to be anticipated that such aprotic solvents will not exhibit enhanced activity.

Lithium aluminum hydride is so reactive that possible solvents are essentially restricted to hydrocarbons, ethers, and tertiary amines. It is insoluble in hydrocarbons and readily soluble in ethers. Unfortunately, no detailed study of its reactions in amine solvents is available. It is generally utilized in ethyl ether, tetrahydrofuran and diglyme as solvents. In these solvents it is a powerful reducing agent, with no significant difference apparent in its reducing power.

Effects of Different Cations

Early observations indicated a marked difference in the reactivity of lithium and sodium borohydrides. Thus sodium borohydride reduces typical esters (such as ethyl acetate and ethyl benzoate) only very slowly, whereas lithium borohydride reduces such esters quite easily (*13*).

In aqueous solution there is no measurable difference in the rate constants for the reactions of sodium and lithium borohydrides with acetone. However, in isopropyl alcohol solution the rate constant for lithium

borohydride is several times greater than that for the sodium salt (*14*). This suggests that the enhancing effect of the lithium ion will be greatest in solvents of low dielectric constant. In such solvents the reaction presumably proceeds through the ion-pair, ($Li^+BH_4^-$), rather than the dissociated ions.

Kollonitsch and his co-workers achieved the successful reduction of simple esters by sodium borohydride in tetrahydrofuran in the presence of lithium and magnesium iodides (*15*). Later they synthesized calcium, strontium, and barium borohydrides, and demonstrated that these borohydrides exhibit an enhanced reducing power over sodium borohydride (*16*).

In our own approach to this problem, we utilized homogeneous solutions of sodium borohydride in diglyme. Thus the addition of an equivalent quantity of lithium chloride or lithium bromide to a 1.0 *M* solution of sodium borohydride in diglyme results in the formation of a precipitate of sodium halide and the formation *in situ* of lithium borohydride. The reagent can be utilized directly, without removing the precipitated salt. At 100°, essentially quantitative uptake of "active hydride" was observed in 1–3 hrs by a number of representative esters: ethyl acetate, ethyl stearate, ethyl benzoate, ethyl cinnamate, and ethyl *p*-chlorobenzoate (*6*). Under the same conditions, sodium borohydride alone brings about only slight reduction of such esters.

Ions of higher ionic potential would be expected to be even more effective. Accordingly we explored the effectiveness of magnesium and aluminum halides in this connection.

Anhydrous magnesium chloride and bromide possess only a small solubility in diglyme (0.013 *M* for magnesium chloride and 0.078 *M* for the bromide, both at 100°). However, the addition of equivalent amounts of the solid salts to diglyme solutions of sodium borohydride brings about the reduction of esters. In this way ethyl stearate was reduced in four hours at 100° to 1-octadecanol in 74% yield and ethyl *p*-nitrobenzoate was reduced in 3–4 hrs at 40–50° to *p*-nitrobenzyl alcohol in 57% yield (*6*).

In pursuing this line of investigation, it was observed that diglyme solutions of aluminum chloride and sodium borohydride, in a molar ratio of 1:3, mix to give a clear solution with no evidence for the formation of the insoluble sodium chloride. Nevertheless, such solutions exhibit markedly enhanced reducing powers (*17*).

At room temperatures, such solutions rapidly reduce aldehydes, ketones, oxides, lactones, acid chlorides, acid anhydrides, esters, acids, nitriles, *t*-amides, azo compounds, and disulfides. No reduction was observed for sodium salts of carboxylic acids, primary amides, nitro derivatives, sulfones, and aromatic nuclei. Consequently, the presence of aluminum chloride has transformed the sodium borohydride from a reagent which in diglyme fails to reduce even ketones at any significant rate to one which exhibits greatly increased reducing power, approaching that exhibited by lithium aluminum hydride itself.

The failure to obtain a precipitate of sodium chloride upon mixing sodium borohydride and aluminum chloride argues against the complete formation of aluminum borohydride in solution.

$$AlCl_3 + 3NaBH_4 \rightarrow Al(BH_4)_3 + 3NaCl\downarrow$$

However, it is possible that the reaction proceeds to produce small equilibrium amounts of aluminum borohydride, with the equilibrium being shifted to completion as the aluminum borohydride reacts with the organic compound.

$$AlCl_3 + 3NaBH_4 \rightleftharpoons Al(BH_4)_3 + 3NaCl$$

Other polyvalent metal halides, such as gallium trichloride and titanium tetrachloride, likewise enhance the reducing power of sodium borohydride. Unfortunately, studies of the full scope of these reagents are not yet available.

A number of aluminohydrides containing cations other than lithium have been synthesized (*4*, *18*). These all appear to be very powerful reducing agents and, on the basis of the available data, it does not appear possible to draw any conclusions as to the effect of the cation on the reducing power of the aluminohydride anion.

Effects of Substituents

The reaction of a typical ketone, such as acetone, with sodium borohydride must involve four successive stages.

$$R_2CO + BH_4^- \xrightarrow{k_2} [H_3BOCHR_2]^-$$

$$R_2CO + [H_3BOCHR_2]^- \xrightarrow{k_2'} [H_2B(OCHR_2)_2]^-$$

$$R_2CO + [H_2B(OCHR_2)_2]^- \xrightarrow{k_2''} [HB(OCHR_2)_3]^-$$

$$R_2CO + [HB(OCHR_2)_3]^- \xrightarrow{k_2'''} [B(OCHR_2)_4]^-$$

The reaction exhibits simple second order kinetics, first order in each component (*7*, *19*). The observed kinetics are consistent with a slow rate-determining reaction for the first stage, with successive stages being considerably faster.

This postulate was confirmed by the preparation of the intermediate, sodium triisopropoxyborohydride, $NaBH[OCH(CH_3)_2]_3$, and the demonstration that its reaction is indeed much faster than the reaction of the ketone with sodium borohydride itself. Thus, the reaction of acetone with sodium borohydride in diglyme is very slow—with no measurable reaction being observed in several hours at room temperature. However, in the same solvent the reaction of acetone with sodium triisopropoxyborohydride is too fast to follow, being complete in a matter of seconds at 0° (*20*).

These results clearly demonstrate that the effect of the alkoxy substituents is to increase the reducing power of the borohydride. Reduction of esters by the reagent was achieved. Unfortunately, the simple alkoxyborohydrides (sodium trimethoxyborohydride and triethoxyborohydride), readily synthesized from sodium hydride and the borate ester in the absence of a solvent, undergo rapid disproportionation in solvents to sodium borohydride and sodium tetraalkoxyborohydride (*21*).

$$(RO)_3B + NaH \rightarrow NaBH(OR)_3$$

$$4NaBH(OR)_3 \xrightarrow{THF} NaBH_4\downarrow + 3NaB(OR)_4$$

This disproportionation renders difficult a quantitative estimation of the effectiveness of these reagents in reducing less reactive functional groups and markedly lessens their utility for such relatively slow reductions.

Alkyl substituted borohydrides, such as lithium trimethylborohydride and sodium triethylborohydride, are readily synthesized (*22*) and prove to be quite stable in solution (*23*). They possess interesting possibilities as selective reducing agents (*23*).

In view of the marked influence of alkoxy substituents upon the reducing power of sodium borohydride, it was of interest to examine the effect of alkoxy substituents on the reducing power of lithium aluminum hydride. Whereas alkyl borates react readily with the alkali metal hydrides to produce the corresponding trialkoxyborohydrides (*22*, *20*), the related reaction with aluminum alkoxides proved to be quite sluggish. However, this reaction has been utilized recently as a synthetic route to sodium triethoxyaluminohydride by treating the "monomeric α-form" of aluminum ethoxide with sodium hydride in tetrahydrofuran in an autoclave at 70–90° (*24*, *25*). In our studies, the treatment of lithium aluminum hydride with alcohols appeared to offer a more convenient route to the trialkoxyaluminohydrides and this procedure was therefore utilized (*26*).

Treatment of lithium aluminum hydride in ethyl ether solution with four moles of methyl, ethyl, or isopropyl alcohol at 25° results in the evolution of four moles of hydrogen and the precipitation of the corresponding lithium tetraalkoxyaluminohydride. However, the addition of four moles of *t*-butyl alcohol results in the formation of only three moles of hydrogen. The fourth mole of hydrogen is evolved only on extended treatment at elevated temperatures.

The reaction product, lithium tri-*t*-butoxyaluminohydride, is only slightly soluble in ethyl ether, but it is readily soluble in tetrahydrofuran and diglyme. Accordingly, the reaction with *t*-butyl alcohol was examined in these solvents. Here also the reaction ceases with the evolution of three moles of hydrogen, with the fourth mole being produced only at elevated temperatures. Consequently, the tendency for the reaction to halt with the formation of the tri-*t*-butoxy derivative cannot be attributed to its low solubility in ether.

Lithium tri-*t*-butoxyaluminohydride proved to be surprisingly stable. A sample in diglyme solution, heated to 165° for 5 hrs, retained 92% of its active hydrogen. It failed to melt below 400° and exhibited signs of decomposition above that temperature. It could be sublimed at 280° at 2 mm pressure.

The failure of lithium tri-*t*-butoxyaluminohydride to react with excess *t*-butyl alcohol at 25° suggested that this reagent should have reducing properties markedly different from those of the parent compound. Accordingly, a number of representative derivatives were treated with the reagent in diglyme solution for 0.5 hr at 0°. Aldehydes, ketones, acid anhydrides, and acid chlorides were completely reduced. However, esters and nitriles were not. Consequently, the reagent is much closer to sodium borohydride than to lithium aluminum hydride in its characteristics.

It was discovered that the reagent is particularly valuable in permitting the reduction of acid chlorides to aldehydes. For this purpose the acid chloride in diglyme or tetrahydrofuran at low temperatures (preferably −78°) is treated with one equivalent of the reagent in the same solvent. The temperature is permitted to rise to room temperature, the reaction mixture poured onto crushed ice, and the aldehyde isolated from the aqueous mixture.

A detailed study of the scope of this study was made (*27*). Aromatic acid chlorides containing substituents in the *meta* and *para* positions form aldehydes in yields of 60–90%. Many types of substituents can be tolerated, including those which might be considered sensitive to reduction, such as nitro, cyano, and carbethoxy.

88%

In some cases, substituents in the *ortho* position tend to reduce the yield: *o*-nitro, 77%, *o*-chloro, 41%.

Polycyclic (α- and β-naphthyl), heterocyclic (nicotinyl), unsaturated (cinnamoyl) and polyfunctional (terphthalyl) acid chlorides may be utilized in this synthesis.

82%

In the case of aliphatic and alicyclic acid chlorides (isobutyryl, adipyl, cyclopropanecarboxyl, fumaryl), the yields fall in the range of 40–60%.

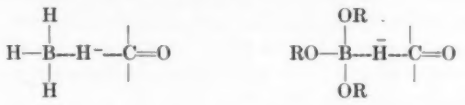
In the synthetic work it is frequently desirable to proceed from some carboxylic acid derivative, other than the acid chloride, to the aldehyde. Consequently, we explored the possibility of converting the dimethylamides and nitriles to aldehydes. In both cases direct treatment with lithium aluminum hydride results in poor yields. Moreover, in neither case does lithium tri-*t*-butoxyaluminohydride react with these derivatives. Fortunately, lithium trimethoxyaluminohydride reacted readily, with moderate yields of aldehyde produced. Better results were realized with lithium diethoxyaluminohydride (*28*). Finally, we have realized optimum results by utilizing lithium triethoxyaluminohydride in ether solution (*29*, *30*).

The procedure is very simple. A 1.0 *M* solution of lithium aluminum hydride in ethyl ether is treated with three moles of ethanol or 1.5 moles of ethyl acetate to form the reagent *in situ* at 0°. To the solution is added one equivalent of the N,N-dimethylamide or the nitrile. After one hour, the reaction mixture is hydrolyzed and the aldehyde is isolated. From the *t*-amide, the aldehydes are generally obtained in yields of 80–90% for both aliphatic and aromatic derivatives. In the case of the nitrile reduction, the yields vary from 70% for aliphatic derivatives to 90% for aromatic derivatives.

The simplicity and wide applicability of these new synthetic procedures should provide valuable new routes from the carboxylic acids to the corresponding aldehydes.

In reductions the lithium trialkoxyaluminohydrides exhibit markedly lower activity than lithium aluminum hydride itself. On the other hand, these alkoxy substituents increase the reactivity of sodium borohydride. It is of interest to consider the basis for this marked difference in the effect of alkoxy substituents in the two systems (*26*).

Reductions by these complex hydrides presumably proceed through a transfer of hydride ion from the anion to the groups undergoing reduction.



On this basis, the transfer of hydride ion from the weaker Lewis acid, alkyl borate, should proceed more rapidly than the transfer from the stronger Lewis acid, borane.

Unfortunately, little is known about the relative strengths of aluminum hydride and aluminum alkoxides as Lewis acids. The polymeric nature of the products renders difficult the experimental comparison of their acid strengths. Fortunately, it is possible to rationalize the observed effect on theoretical grounds.

In the case of both the alkyl borates and the aluminum alkoxides, the electron-withdrawing inductive effect of the alkoxy groups would be expected to increase the acid strengths of the two related derivatives, $(RO)_3B$ and $(RO)_3Al$. However, large resonance contributions in the alkyl borate satisfy the electron deficiency of the boron atom and reverse the anticipated electronic effect of the alkoxy groups.

Consequently, instead of being strong Lewis acids, alkyl borates are quite weak.

Such resonance interactions should be far less important in a second row element, such as aluminum, than in a first row element, such as boron. It would not be unexpected if the electronic effect of the alkoxyl groups in aluminum derivatives were primarily a reflection of the electronic-withdrawing inductive effect of these groups with only minor modifications by the less important resonance interactions. In this way the markedly different effects of alkoxy substituents on the reducing powers of the borohydride and aluminohydride derivatives are the result of the different capacity of boron and aluminum to participate in resonance interactions involving double-bonded structures with the oxygen atom of the substituent.

Electrophilic Reductions

Reductions by alkali metal borohydrides and aluminohydrides appear to involve a transfer of hydride ion from the anion to an electron-deficient center of the functional group.

The ability of diborane to function as a reducing agent was recognized long ago (*31*). However, diborane is a strong Lewis acid. Consequently, in the molecule it must preferentially attack those centers high in electron density. This reasoning suggested an examination of the relative susceptibility toward diborane of various functional groups as contrasted to their behavior toward borohydride (*32*).

Because of the high solubility of diborane in tetrahydrofuran, such solutions are conveniently utilized for reductions by diborane. Alternatively, it is often possible to generate diborane *in situ* from the reaction of sodium borohydride and boron trifluoride-etherate.

Both aliphatic and aromatic aldehydes and ketones are rapidly reduced at room temperature. However, chloral is stable toward the reagent (*31*). Lactones and oxides reduce readily. Esters react only slowly. Acid chlorides and sodium salts of carboxylic acids are not reduced. Nitro compounds do not react. Perhaps the most interesting development is the observation that both carboxylic acids and nitriles are rapidly reduced by the reagent.

A study of the relative reactivity of a number of groups toward diborane indicates the following order of reactivity:

carboxylic acids > ketones > nitriles > epoxides > esters > acid chlorides (*33*).

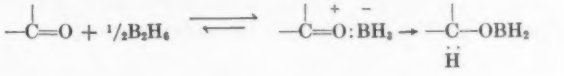
Toward alkali metal borohydride the order is:

acid chlorides > ketones > epoxides > esters > nitriles > carboxylic acids.

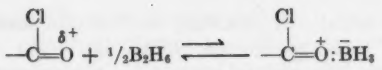
Although not within the scope of the present discussion, it is worth noting that olefins are highly reactive toward diborane (falling between carboxylic acids and ketones in the former reactivity series), but are highly inert toward the alkali metal borohydrides.

With such markedly different reactivities, it is apparent that the judicious use of either diborane or alkali metal borohydride permits the reduction of one group in the presence of a second, or the reverse operation.

It was previously noted that carbonyl groups of simple aldehydes and ketones react rapidly with diborane, whereas the carbonyl groups of chloral and acid chlorides are relatively inert to the hydride (*31*). It was considered significant that those aldehydes and ketones which react readily with diborane also form stable addition compounds with boron trifluoride, whereas chloral and acetyl chloride add this Lewis acid only with difficulty at low temperatures (*31*). It was suggested that the initial stage of the reaction with the carbonyl group involves an acid-base interaction, with borane adding to the oxygen atom, followed by a transfer of a hydride unit from boron to carbon.



On this basis, the inertness of acetyl chloride and of chloral toward diborane was attributed to the decreased basic properties of the oxygen atom of the carbonyl group, resulting from the powerful inductive effects of the halogen substituents.

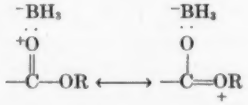


It is noteworthy that both acetyl chloride and chloral are highly reactive toward sodium borohydride. It is not unreasonable that the electron deficiency induced by the chlorine substituents, which serves to inhibit attack by the Lewis acid diborane, should facilitate attack by the nucleophilic borohydride ion.

In other words, diborane is a Lewis acid which functions best as a reducing agent in attacking groups at positions of high electron density, whereas borohydride is a Lewis base which prefers to attack functional groups at positions of low electron density.

This interpretation can be extended to account for the behavior of nitriles. The nitrile group is relatively insensitive to attack by nucleophilic reagents. Consequently, its relative inertness toward attack by borohydride ion is not unexpected. However, the nitrogen atom of the nitrile group is relatively basic. It adds boron trifluoride to form addition compounds of moderate stability. Presumably, the rapid reduction of nitriles by diborane involves an initial attack of the reagent at this relatively basic position.

Two factors presumably account for the relatively slow rate of reduction of carboxylic esters. First, addition of the borane particle to the oxygen atom of the carbonyl group must compete with addition to the oxygen atom of the alkoxy group. Second, transfer of hydride from boron to carbon will presumably be hindered by the stabilization provided the carbonyl group by resonance with the oxygen atom of the alkoxy group.

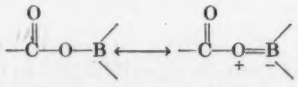


The fast rate of reaction of diborane with carboxylic acids remains to be considered. The first stage in this reaction appears to be the formation of a triacylborane (*32*).

$$3RCO_2H + {}^1/_2B_2H_6 \rightarrow (RCO_2)_3B + 3H_2$$

This initial reaction product is readily reduced by further treatment with diborane. Indeed, the carboxylic acid group in this intermediate is so active that reduction by sodium borohydride is also observed.

The following interpretation of this interesting phenomenon is proposed. The electron deficiency of the boron atom in the triacylborane should exert a powerful demand on the electron pairs of the acyl oxygen. Such resonance as occurs will involve interaction of this oxygen atom with the boron atom, rather than the usual resonance with the carbonyl group.



According to this interpretation, the carbonyl groups in the triacylboranes should resemble those in aldehydes and ketones far more than the less active carbonyl groups of esters.

It is possible to produce a number of functional derivatives of diborane, such as the dichloroborane etherate (*34*) and bis-3-methyl-2-butylborane (*35*).

$$B_2H_6 + 4BCl_3 + 6(C_2H_5)_2O \rightarrow 6Cl_2HB{:}O(C_2H_5)_2$$

$$B_2H_6 + 4(CH_3)_2C{=}CHCH_3 \rightarrow 2[(CH_3)_2CHCH(CH_3)]_2BH$$

Preliminary observations on the latter reagent indicate interesting possibilities. Thus bis-3-methyl-2-butylborane reduces aldehydes and ketones, but fails to reduce carboxylic acids. Thus, in contrast to diborane the reagent permits the reduction of ketones in the presence of the reactive carboxylic acid group. Bis-3-methyl-2-butylborane does not react with esters, but it does react in a 1:1 ratio with γ-lactones. Thus it is an excellent reagent for converting γ-lactones into γ-hydroxyaldehydes (*36*).

These interesting results with diborane and the substituted boranes suggest the desirability of a systematic study of the reducing properties of aluminum hydride and its substitution derivatives. Individual observations are available, but a systematic survey has not yet been described.

Thus the addition of aluminum chloride to lithium aluminum hydride, presumably with the formation of chloroaluminohydrides *in situ*, brings about a conversion of aryl ketones into the corresponding arylmethanes (*37*), and markedly improves the yield of bromohydrin in the reduction of 3-bromoacids and esters (*38*). The same reagent reduces acetals and ketals to the corresponding ethers (*39*) and cyclic ethers and acetals to the corresponding hydroxyethers (*40*).

Selective Reductions

As has been pointed out, these new reagents permit many selective reductions. Moreover, by a judicious choice of reducing agent it is frequently possible to reduce one group in the presence of a second, and often to carry out the reverse operation.

In order to let the reader become acquainted with the main possibilities, Table 1 summarizes the observed reactivities of the main functional groups toward these reagents. The symbol (+) indicates a rapid reaction at 25–75°, correspondingly, the symbol (−) indicates slow or insignificant reaction under these conditions. No symbol indicates that no quantitative observation has yet been reported for the case in question.

From this summary, it is evident that sodium borohydride will permit the reduction of an acid chloride group in the presence of an ester grouping, whereas diborane will reduce the ester in the presence of the acid chloride grouping. Similarly, lithium borohydride will reduce the nitrile group in the presence of the ester group, whereas diborane will do the opposite. With these reagents it is simple to reduce a carboxylic acid group without attack on a nitro substituent. The possibility for numerous other selective reductions is indicated by the summary.

Conclusion

From this survey it is evident that rapid progress has been made in developing new selective reducing agents

which greatly simplify the synthetic problems of the organic chemist. Much has been done, yet much remains to be done. It is clearly possible that the continued research in this area will make available specific reagents which will make feasible the reduction of almost any specific functional group in the presence of any other functional group. With the growth of our understanding of the influence of structure on reactivity in this area, it may be hoped that we shall be in position to design reducing agents to perform desired reductions much as Nature has developed enzymes to accomplish highly specific reactions.

Table 1. Summary of Behavior of Various Functional Groups Toward the Hydride Reagents

	$NaBH_4$ in ethanol	$NaBH_4$ + LiCl in diglyme	$NaBH_4$ + $AlCl_3$ in diglyme	$NaBH_4$ + BF_3 in diglyme	B_2H_6 in tetrahydrofuran	Bis-3-methyl-2-butylborane in THF	$LiAlH(O\text{-}t\text{-}Bu)_3$ in THF	$LiAlH(OMe)_3$ in THF	$LiAlH_4$ in ether
Aldehyde	+	+	+	+	+	+	+	+	+
Ketone	+	+	+	+	+	+	+	+	+
Acid chloride	+	+	+	+[a]	−	−	+[e]	+	+
Lactone	+	+	+	+	+	+[c]		+	+
Oxide	−	+	+	+	+	−		+	+
Ester	−	+	+	±[b]	±[b]	−	−	+	+
Carboxylic acid	−	−	+	+	+	−[d]		+	+
Carboxylic salt	−	−	−	−	−				+
Nitrile	−	−	+	+	+	+	−	+	+
Nitro	−	−	−	−	−	+			+
Olefin	−	−	+	+	+	+	−	−	−

[a] Fast reaction with the sodium borohydride prior to addition of the boron trifluoride.
[b] Moderate reaction with longer reaction times.
[c] Reaction in a 1:1 ratio.
[d] Reaction to form derivative, RCO_2BR_2, but no reduction.
[e] Yields aldehyde with reverse addition.

Finally, the writer was invited to review for this symposium the work of his research group in the field of New Selective Reducing Agents. In doing so, it was not possible within the time permitted to do adequate justice to the work in this area of many other research groups. It is hoped that a detailed review in the near future will make it possible to describe in detail all of the interesting developments in this active field, from the research group at Purdue University and also those at other institutions.

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Charles B. Colburn
Redstone Arsenal Research Division
Rohm & Haas Company
Huntsville, Alabama

Recent Developments in N—F Chemistry

The purpose of this paper is twofold: to point out recent developments in the chemistry of compounds containing the N—F bond and to illustrate the absolute necessity of proper instrumentation in carrying out modern inorganic chemical research.

Nitrogen Trifluoride and Fluorine Azide (NF_3 and FN_3)

The first fluoride of nitrogen to be prepared was nitrogen trifluoride (NF_3), in 1928 by Otto Ruff (*1*) of Germany after 25 years of experimentation. [Ruff's first reported attempt to prepare a fluoride of nitrogen was in 1903 (*2*).]

Nitrogen trifluoride was prepared by the electrolysis of molten ammonium bifluoride. Ruff also reported that difluoramine (HNF_2), fluoramine (H_2NF) and a compound NF_2 were also prepared by this electrolysis. It has recently been shown that these identifications were incorrect. However, it is to his credit that (in the absence of vapor phase chromatography, mass-, infrared-, nmr- and epr-spectroscopy), he was able to identify any of the components of the complex gaseous mixture produced by this electrolysis.

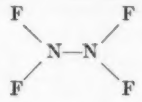
In 1942, Haller (*3*) of Cornell prepared fluorine azide (FN_3) from the reaction of hydrazoic acid with fluorine. Fluorine azide proved to be an extremely unstable compound which decomposed spontaneously to yield difluorodiazine (N_2F_2) and nitrogen. Bauer (*4*) at Cornell studied the electron diffraction of difluorodiazine and found it to be composed of *cis* and *trans* isomers.

Tetrafluorohydrazine (N_2F_4)

Work in the N—F field was quiescent for 11 years until 1958 when Colburn and Kennedy (*5*) of Rohm and Haas Company, Redstone Research Division, reported the synthesis of tetrafluorohydrazine from the thermal reaction of nitrogen trifluoride with various fluorine acceptors such as copper, bismuth, arsenic, antimony, and stainless steel. The boiling point of tetrafluorohydrazine is −73°C and its critical temperature is 36°C. From an extrapolation of the vapor pressure data a critical pressure of 77 atm is estimated.

The infrared absorption spectrum of tetrafluorohydrazine consists of a very strong complex band between 9.75 and 10.75 μ and a strong broad band at 13.06 μ.

The mass spectrum of tetrafluorohydrazine given in Table 1 is consistent with the proposed structure:



The F^{19} nuclear magnetic resonance spectrum of tetrafluorohydrazine consists of a single broad unresolved band at a field of approximately 75 ppm lower than that of the F^{19} nuclei of trifluoroacetic acid.

Armstrong (*6*) and co-workers at the National Bureau of Standards have determined the heat of formation of tetrafluorohydrazine and found it to be -2.0 ± 2.5 kcal/mole.

Table 1. Fragmentation Pattern of N_2F_2

M/e	Ion	Pattern (%)
52	NF_2^+	90.6
33	NF^+	100.0
28	N_2^+	7.7
19	F^+	4.7
14	N^+	8.5

Recently Loughran and Mader (*7*) of Los Alamos Scientific Laboratory have reported an estimated bond dissociation energy of the N—N bond in tetrafluorohydrazine of approximately 30 kcal from appearance potential measurements.

Lide and Mann (*8*) of the National Bureau of Standards have studied the microwave spectrum of tetrafluorohydrazine and report that the observed rotational constants are consistent with a hydrazine-like model (point group C_2).

Recently several other methods of preparation of tetrafluorohydrazine have been described. Frazer (*9*) of the Ernest O. Lawrence Radiation Laboratory has prepared tetrafluorohydrazine from the homogeneous reaction of nitrogen trifluoride with mercury in an electric discharge. Lawton and Weber (*10*) of Rocketdyne have found that tetrafluorohydrazine is formed when difluoramine (HNF_2) is reacted with various solids (i.e., LiH). Morrow and co-workers (*11*) at Reaction Motors Division of Thiokol have found that the fluorination of ammonia in a packed reactor produces tetrafluorohydrazine.

Difluoramine (HNF_2)

As mentioned above, Ruff (*12*) reported the formation of difluoramine from the electrolysis of molten ammonium bifluoride. This work has never been confirmed

Presented as part of the Symposium on Recent Advances in Inorganic Chemistry, sponsored jointly by the Divisions of Inorganic Chemistry and Chemical Education, at the 137th Meeting of the ACS, Cleveland, Ohio, April, 1960.

This work was performed under the sponsorship of the Army Ordnance Corp. Contract No. DA-01-021 ORD-5135.

and indeed, Burg (*13*) has pointed out the uncertainty of the identification.

Difluoramine was first prepared by Kennedy and Colburn (*14*) in 1959. The observed trace amounts of difluoramine formed during the preparation of tetrafluorohydrazine by the passage of nitrogen trifluoride (saturated with water vapor) over elemental arsenic at 250–300°C. This preparation of difluoramine suggested the intermediacy of tetrafluorohydrazine and arsine. Further experiments have established the fact that the reaction between arsine and tetrafluorohydrazine does indeed yield difluoramine (*15*). Difluoramine has also been prepared in yields up to 75% by the reaction of tetrafluorohydrazine with mercaptans (*15*).

Difluoramine has recently been reported arising as a by-product of two fluorination reactions: from the fluorination of urea and subsequent decomposition of intermediate products (*16*), and from the fluorination of ammonia (*17*).

Difluoramine is a colorless gas at room temperature. Its boiling point is −23°C and its heat of vaporization is estimated to be 5940 cal/mole. Its melting point is approximately −116°C and its critical temperature (by the Cagniard de la Tour tube method) is 130°C.

The infrared absorption spectrum of difluoramine consists of strong doublets at 7.0, 7.8, 10.2 μ and a triplet at 11.2 μ. The nmr proton spectrum consists of a triplet, as would be expected from a proton spin-spin coupling with two equivalent fluorine nuclei. The center of the triplet is approximately 6 cycles on the high field side from benzene. The spin-spin splitting is about 24 cycles. The fluorine resonance spectrum consists of two broad bands arising from spin-spin coupling of the fluorine nuclei with the proton. The high field member of this doublet was measured at 2100 cycles on the low field side of trifluoroacetonitrile.

The mass spectrum of difluoramine is given in Table 2. The spectrum was obtained on a Consolidated Electrodynamics Model 620 Spectrometer.

Table 2. Fragmentation Pattern of HNF_2

M/e	Ion	Pattern (%)
53	HNF_2^+	100.0
52	NF_2^+	8.7
34	HNF^+	99.5
33	NF^+	47.4
20	HF^+	4.0
19	F^+	5.2
15	NH^+	8.7
14	N^+	23.0

Difluorodiazine (N_2F_2)

Haller's preparation of difluorodiazine (*3*) from the thermal decomposition of fluorine azide is not a convenient one because of the danger of explosions during runaway decompositions. Colburn, *et al.* (*18*) recently found that difluorodiazine can be prepared by the electrolysis of molten ammonium bifluoride. This observation has been confirmed by Schmeisser (*19*). Difluorodiazine is a minor product [5–10% of the condensable (in liquid nitrogen) gases] from the electrolysis of molten (120–130°C) ammonium bifluoride.

As reported by Bauer (*4*), the difluorodiazine exists in at least two isomeric forms, supposedly, *cis*- and *trans*-difluorodiazine. Fleeting evidence for a third isomeric form of N_2F_2 has been reported (*18*). At the present time there is some question as to the identification of the structure of the two isomers which have been isolated. The present discussion assumes that the isolated isomers are *cis* and *trans* difluorodiazine.[1]

A third method of preparation of difluorodiazine has been reported by Frazer (*5*). Difluorodiazine is produced (along with tetrafluorohydrazine) by the homogeneous reaction of nitrogen trifluoride with mercury in an electric discharge. Morrow *et al* (*17*), also observed difluorodiazine as a product of the fluorination of ammonia.

Low temperature distillation and vapor phase absorption chromatography are the best purification methods for difluorodiazine. The *trans* isomer has been obtained in a purity of 99.7% by chromatography and the *cis* isomer has been obtained by low temperature distillation in a minimum purity of 97.5%.

Both physical and chemical properties of the two isomers are quite different as can be seen from the information in Table 3. The mass spectra of the *cis* and *trans* isomers of difluorodiazine are shown in Table 4. The F^{19} nmr spectra of the isomers were observed and are given in Table 5.

Table 3. Physical Properties of *Cis* and *Trans* Difluorodiazine

Property	*Cis*	*Trans*
Vapor pressure equation	log Pmm = $-803.0/T + 7.675$	log Pmm = $-742.3/T + 7.470$
Boiling point (°C)	−105.7°	−111.4°
Heat of vaporization (cal/mole)	3670	3400
Critical temperature (°C)	−1°	−13°
Critical pressure (estimated atm)	70	55
Melting point (°C)	Below −195°	−172°

The infrared spectrum of the *trans* isomer in the rock salt region showed a single p-q-r band centering at 10.05 μ while the *cis* isomer showed much more complex absorption with a strong p-q-r band centering at 10.48 μ and a strong p-r band at 11.07 and 11.33 μ and a very strong p-q-r band centering at 13.57 μ. Also weak doublets at 6.52 μ and 6.62 μ were observed.

Table 4. Mass Spectral Cracking Pattern of *Cis* and *Trans* Difluorodiazine

M/e	Ion	*Cis* N_2F_2 (%)	*Trans* N_2F_2 (%)
66	$N_2F_2^+$	0.5	25.3
47	N_2F^+	100.0	43.4
33	NF^+	6.0	5.0
28	N_2^+	84.5	100.0
23.5	N_2F^{++}	1.4	...
19	F^+	5.3	1.8
14	N^+	10.5	11.6
Sensitivity of highest peak div./μ		12.36	22.36

[1] A recent report from Lawrence Radiation Laboratory, University of California, Livermore, UCRL-5541 (March 30, 1960), by R. H. Sanborn, presents some spectral evidence concerning the structure of the two isolated isomers. The report confirms the assignment of the *trans* isomer but supports the 1,1-difluorodiazine structure for the other isolated isomer. The question is still unresolved; but until it is resolved we shall refer to the second isomeric form as the *cis* isomer.

Table 5. NMR Spectra of *Cis* and *Trans* Difluorodiazine

Compound	δ (cycles from CF_3COOH)	J_{N-F} (cycles)
N_2F_2 (*cis*)	8320	107
N_2F_2 (*trans*)	6690	53

The chemical reactivities of the *cis* and *trans* isomers are quite different. *Cis* N_2F_2 reacts slowly (completely in two weeks) with glass to form silicon tetrafluoride and nitrous oxide at room temperature and high pressure while the *trans* isomer is essentially unchanged after a month in a sealed glass tube at room temperature. Mercury reacts much more rapidly with the *cis* isomer than with the *trans*. When heated, the *trans* isomer is converted into the *cis;* the heat of isomerization is 27.5 ± 5.0 kcal/mole (*18*).

An extremely interesting reaction of difluorodiazine is its catalytic effect on polymerization of various monomers. It has been observed that a pressure of 300 mm of N_2F_2 over the monomers of methyl methacrylate, styrene, and cyclopentadiene led to their polymerization in twelve hours or less at room temperature. Difluorodiazine also catalyzed the polymerization of tetrafluoroethylene at 125°C. At temperatures in the neighborhood of 140°C. polymeric substances were formed in the presence of difluorodiazine with ethylene and propylene. At least in the case of methyl methacrylate, the *cis* isomer is more effective in catalyzing polymerization than is the *trans* isomer.

Chlorodifluoramine (NF_2Cl)

Petry (*20*) found in 1960 that when equimolar quantities of difluoramine and boron trichloride are condensed *in vacuo* at −130°C they form a white solid which is stable at −80°C. When the solid is warmed toward room temperature, decomposition of the solid yields hydrogen chloride (HCl), chlorine (Cl_2), and a new compound, chlorodifluoramine (NF_2Cl).

Chlorodifluoramine is a colorless gas. Its vapor pressure curve is given by the equation

$$\log \text{Pmm} = \frac{-950}{T} + 7.478.$$

The extrapolated boiling point is −67°C. The heat of vaporization calculated from the above equation is 4350 cal/mole. The melting point of chlorodifluoramine has not been obtained but lies between −183° and −196°C.

The mass spectrum of chlorodifluoramine is given in Table 6.

The infrared spectrum of chlorodifluoramine consists of very strong bands centered at 10.8 (triplet), 11.7 (doublet), and 14.4 μ (triplet); a doublet of moderate intensity centered at 13.4 μ and weak bands at 5.4, 5.7, 5.9, and 7.3 μ.

The F^{19} nmr spectrum of chlorodifluoramine consists of a single broad band centered at 8685 cycles to the low field side of trifluoroacetic acid.

Uses of N—F Compounds

The only use of N—F compounds reported in the literature is the use of nitrogen trifluoride with hydrogen in a torch (*21*). This torch can weld, braze, and cut metals without additional flux since the nitrogen trifluoride acts as a gaseous flux.

Table 6. Mass Spectral Cracking Pattern of Chlorodifluoramine

M/e	Ion	Pattern (%)
14	N^+	3.8
19	F^+	1.6
33	NF^+	37.1
35	Cl^+	21.9
37		6.5
49	NCl^+	30.1
51		
52	NF_2^+	100
68	$BFCl^+$	26.2
70		22.4
72	Cl_2^+	8.5
74		1.3
87	NF_2Cl^+	46.4
89		14.5

Summary

A group of very interesting simple molecules have recently been synthesized and studied: tetrafluorohydrazine (N_2F_4), difluoramine (HNF_2), chlorodifluoramine (NF_2Cl) and *cis* and *trans* difluorodiazine (N_2F_2). The further investigation of these compounds should be of great benefit to the understanding of molecular structure and chemical bonding.

CAUTION: Numerous explosions have occurred in work with these compounds. Reference is made to the original literature for experimental precautions to be used with these materials.

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Otto L. Forchheimer
and **Terry F. Newkirk**
Trionics Corporation
Madison, Wisconsin

Recent Advances in Solid State Inorganic Materials

Materials affect progress in two ways: Either the properties of available materials suggest new applications or the unavailability of suitable materials retards inventive possibilities. The first effect is illustrated by the slow development of tools and utensils which followed the discovery of bronze. Not only did bronze, and later iron, make possible a variety of aids to man; they were essential to the development of civilization. The retarding effect of the lack of a material, on the other hand, is very evident in the limitations imposed on today's rapidly advancing technologies; we often hear a statement such as "If there were only a rubber-like material I could use at 2000°." This second effect, however, is not peculiar to the present. For example, reflection on the possible inventions which Leonardo da Vinci could have made if he had known our modern materials staggers the imagination.

The very rapid strides in such diverse fields as high-temperature technology and electronics during the last several decades, to cite but two examples, have been a severe drain on our storehouse of materials. The re-entry problems of space exploration, the extreme operating temperatures of jet and nuclear engines and power plants, applications of solar energy, and the increased efficiency of some processes at higher temperatures impose severe demands for materials of greater temperature resistance. In electronics, the need is for materials which will permit the achievement of miniaturization, greater reliability, and longer life in electronic hardware.

For these and other fields, the scientists who deal with materials are continually asked for substances which will perform under an ever-increasing extremity of conditions or which have a specified combination of a number of very desirable properties. In some instances, the needed materials are at hand. Many times, however, materials which only approximate the desired properties or which are, at best, only substitutes have to be used. One illustration is the use of ablative plastic materials because of the lack of materials which can withstand both high temperature and strong thermal shock. In still other instances, the development of certain devices has been limited by the properties of available materials. For example, the power of present jet engines is limited to the level permitted by the temperature and thermal shock properties of the materials which can be used to construct or line the parts of the engine.

The demand for new and modified materials has been increasing with the increased defense effort. Materials research has been given high priority along with other necessary developments. The needs of the design engineers have been translated into the specifications on which the materials engineer bases his development work. Basic research in such fields as inorganic polymer synthesis, solid state reactions, and theory of electronic properties of molecules are being supported by various government agencies. More effort is being channeled toward development in such special areas as metal whisker formation, superalloys, high-purity materials, and magnetic properties of materials. Thus, the search for new and improved materials is being carried out on many fronts, although lack of coordination between the different laboratories engaged in this search is still somewhat of an obstacle to rapid progress.

Some of the more stringent requirements which we are facing for materials are listed in Table 1. Approaches to these requirements may be provided by recent advances involving the discovery of new properties and uses of known materials as well as the development of new materials with improved properties.

Table 1. Important or Desired Properties of Materials

Properties for high-temperature structural use:
- Strength at elevated temperatures
- Low density
- Thermal shock resistance
- Chemical stability

Properties for other high-temperature uses:
- Ductility
- Elasticity
- Chemical stability (especially oxidation resistance)
- Strength
- Thermal shock resistance

Properties for electronic applications:
- Semiconductor materials:
  - High carrier mobility, Low dielectric constant } (for high frequency response)
  - Wide band gap, High melting point } (for increased temperature performance)
- Ferroelectric materials:
  - Controlled dielectric constant
  - Good dielectric strength
  - Low loss factor
  - Curie temperature and piezoelectric properties

Other desirable properties:
- Stronger ceramic bodies
- Resistance to environment (nuclear, climate, etc.)
- Better insulating characteristics (thermal and electrical; resistance to breakdown by electrical discharge)
- Solid lubricants with higher temperature resistance
- High purity

New Properties and Uses of Known Materials

Whenever a need arises for a material with a certain set of defined properties, the known materials are surveyed. There is often great difficulty in selecting materials, however, because little information is available in a language understood by the design engineer.

Presented as part of the Symposium on Recent Advances in Inorganic Chemistry, sponsored jointly by the Divisions of Inorganic Chemistry and Chemical Education, at the 137th Meeting of the ACS, Cleveland, Ohio, April, 1960.

Too few classes of materials have been surveyed in terms of their engineering properties; many materials have been tested for only a special class of properties, often aimed at a particular application or industry. Even if manuals on material properties were available, the newest materials would take considerable time to find their way into them. There has been a movement lately in some government agencies to sponsor the compilation of design data handbooks in a variety of materials classifications. These would greatly aid in finding appropriate known materials for various applications. An additional service of great value would be the establishment of a national materials evaluation laboratory, to test new materials and new material combinations for properties and purposes other than those for which they were developed or for which they had already been evaluated. Such a laboratory might also issue handbooks, preferably in loose-leaf form, which would be continuously revised.

Silicon Carbide

A good example of a material which is sufficiently versatile for uses in many areas is silicon carbide. Many of these uses have been explored only recently; others have been known for some time. After its discovery in 1891, the hardness, highly refractory nature, and relative inertness of silicon carbide were soon recognized. It was first used as an abrasive and has continued to be a successful one. Also relatively early in its history, silicon carbide in powdered form was found to act as a non-linear resistor. Later, when the temperature dependence of the resistance was determined, the now familiar silicon carbide heating unit was developed.

Silicon carbide is used in the metallurgical industry because it dissociates in molten iron and serves to deoxidize the melt. The activity in silicones helped to bring about a chemical application of silicon carbide, as a starting material in their synthesis. When silicon metal in very pure form was required for semiconductors, silicon carbide was considered a likely source since it is readily purified of certain metallic contaminants. Silicon tetrachloride, obtained by the chlorination of silicon carbide, is an easily liquefied vapor, thus lending itself to further purification. Recent investigations of the chlorination of silicon carbide have led to another interesting material. The carbon residue after complete chlorination has been found to be entirely amorphous, with no X-ray pattern at all, and completely free of the hydrogen or oxygen which accompanies organically derived carbons. So far, no actual uses have been found for this new carbon despite its unusual properties.

The use of silicon carbide in structural applications requiring a refractory and abrasion resistant material developed more slowly here than in Europe. The lag was due partly to cost considerations and partly to more stringent requirements in effect by the time silicon carbide was introduced for this purpose: the clay binders used to manufacture bricks from silicon carbide were undesirable because purity (for inertness) and ability to reach theoretical temperatures had become important. Sintering and hot pressing techniques for making high-purity structural forms from silicon carbide were not easily developed but are now known. Both self-bonded silicon carbide and a silicon nitride-bonded material are now produced. The excellent thermal conductivity of silicon carbide has led to its use where heat must be dissipated or transmitted rapidly, as in combustion chambers and muffles.

Electrical uses of silicon carbide are presently in the forefront. The previously mentioned non-linear resistivity of silicon carbide has made it of interest for varistors, devices which are similar in many aspects to lightning arrestors but utilized for considerably lower and controlled voltage ranges. The lack of knowledge about the mechanism of silicon carbide resistivity has made it difficult to control this property and to achieve varistors of controllable voltage ranges. Despite this difficulty, varistors have found wide use in telephone equipment to protect switch gear and other circuit parts from voltage surges. The resistive properties of silicon carbide are still a very fertile field for study and could produce some interesting results. They can be attributed to some extent to the innate resistivity possessed by silicon carbide as a semiconductor. The contact resistance between particles pressed together at a certain pressure, as in the formation of varistors, also contributes. Impurities affect both of these variables, but not necessarily in the same way.

Silicon carbide is also being investigated as a material for transistors and other semiconductor devices (see later discussion of electronic materials), for thermistors (because of its considerable temperature coefficient of resistivity), and for rectifiers (its rectification properties may be due to oxidized surface layers). Other interesting uses may be derived from its luminescent properties when high-voltage probes are applied to a surface covered with an oxidized silicon carbide film.

Thus, we have in silicon carbide a material which already has a multiplicity of uses and yet still remains a mystery as far as a number of its properties are concerned. Many new uses are promised by the exploration of these properties.

Pyrolytic Graphite

Since a new form of carbon was mentioned in connection with the discussion of silicon carbide, a word is in order about an already known but neglected form which has recently been resurrected. This material is pyrolytic graphite—graphite which is deposited in layers from the gas phase (decomposition of hydrocarbons). It has been produced in the laboratory for many years in minute quantities, e.g., as a thin coating on a hot filament, but has only recently become available in commercially usable sizes. Pyrolytic graphite is an unusual material which provides strongly anisotropic thermal and electrical conductivity characteristics. It has thermal and electrical conductivities several orders of magnitude higher in the plane parallel to the surface than at right angles to the surface. The extent of the anisotropy of the electrical conductivity is controllable by the conditions of preparation of the pyrolytic graphite; it is 1000:1 for the material deposited at 2000°C.

This oriented graphite is expected to be useful for extremely high-temperature applications in rockets and missiles, electrical and electronic systems, and

nuclear reactors. Typical properties of pyrolytic graphite are compared in Table 2 with those of two other materials presently used in such applications.

Table 2. Typical Properties of Pyrolytic Graphite[a]

Property	Pyrolytic graphite	Graphite	Alumina (Al_2O_3)
Sublimation or melting point	3678°C (6650°F)	3678°C (6650°F)	2150°C (3870°F)
Thermal conductivity (Btu/hr/sq ft/°F/ft)	a = 92.5–225.4 c = 1.16–2.02[b]	109.2	17.3
Electrical resistivity (ohm-cm)	a = 200–250 × 10^{-6} c = 0.25	800 × 10^{-6}	10^{16}–10^{18}
Hardness (Mohs)	a = 1.0 c = 4.5	0.5–1.0	9.0
Strength/density (approximate) (1000 psi)	10	1.34	7.55

[a] Reference: Materials in Design Engineering **51**, No. 2, 16 (1960).
[b] Absolute value depends on density.

Ductile Ceramics

When known materials are surveyed for any particular purpose, their shortcomings often show up immediately. For example, when high-temperature structural materials are required, under temperature or oxidizing conditions which do not permit the use of metals or superalloys, the ceramic materials are naturally considered. Yet their brittleness and generally poor thermal shock resistance are known even before they are tried.

There is some hope that the brittleness of ceramics is not inherent and might be overcome. This feeling is engendered by the long-known fact that some ionic materials are ductile under certain conditions (e.g., NaCl in warm water or AgCl protected from exposure to light). Further encouragement of this point of view has come from investigations which showed that MgO bars cleaved from single crystals are very ductile.

Extensive work is presently being carried out from various approaches to arrive at the basic conditions under which ceramics are ductile as well as the conditions under which they become embrittled. Both dislocation mobility and surface effects are being screened for their relationship to ductility and brittleness. Brief mention of some of the observations made in respect to surface effects will indicate the interesting progress in this work. A saturated solution of salt was found to render NaCl crystals brittle, while a saturated KCl solution had no effect on their ductility. Water appeared to have no effect on MgO, but embrittled MgO was made ductile again by dissolving off the surface layer with dilute HCl. De-aerated water did embrittle MgO, indicating that water may have an embrittling action which is inhibited by the dissolved, slightly acid CO_2.

Similar surface and atmosphere effects have been observed for "dirty ceramics," i.e., multiphase polycrystalline materials. For example, a number of investigators found that the presence of water vapor lowered the strength (or increased the brittleness) of such materials by 20–30%. Utilizing a coating which not only was impervious to water but also put the ceramic materials under compression increased their strength. One other recent result may be particularly important in view of the emphasis placed on the necessity for pure materials in many discussions of the ductility of "brittle" solids. We have observed enhanced ductility resulting from the addition of certain other substances. When small amounts (0.1–1.0%) of such substances as barium titanate and potassium dichromate were added to silver chloride, greater elongations were attained in tensile specimens under test. By a combination of such addenda and careful annealing, ordinary polycrystalline (fuse-cast) reagent-grade silver chloride may become useful for a variety of applications requiring a ductile material.

Factors in Development of New or Improved Materials

The experimental use of materials in new applications often points out other required properties or modifications which may or may not have been foreseen. As an example, we may cite some of the problems which accompanied the miniaturization of electrical circuits and components. Small units had greater difficulty in dissipating heat. Corona discharge through insulating media—not considered serious in larger circuitry—also became a major problem in these units. Dielectrics and other materials which would not allow corona discharge suddenly became an important materials requirement, giving impetus (to mention one important area) to developments in the silicone field.

The use of new materials and new processes in turn calls for additional new materials and techniques. When some of the newer metals such as titanium and zirconium came into prominence, machinists had difficulty finding the proper abrasive tools with which to grind them. Grinding wheels wore away a great deal more rapidly than the metals. It turned out that a new and still largely untried abrasive material, zirconium oxide, did a better job.

The preceding example illustrates another important aspect of the search for materials. This is the lack of basic work to support development and application. To find a new abrasive material is a big order simply because the basic mechanism of the abrasion process and the role which the abrading materials play are still largely unknown. Thus, trial and error is the main method of discovering new abrasive substances, tempered only by the experience of the abrasion technologists. This lack of basic knowledge is not confined to the field of abrasives but exists in many areas of materials development. It is encouraging to note, however, that at least in some areas basic knowledge is being ferreted out concurrently with more specific development work. For example, while much development work is being done on the few known inorganic high-temperature materials with some ductility, a program leading to a more fundamental understanding of the mechanism of plastic flow in crystals and related phenomena is receiving considerable attention and support from the same agencies which encourage the development phases of the over-all program. Nevertheless, the storehouse of basic information on which we can draw when we desire to develop a material for a particular application is rarely sufficiently stocked.

One parameter which has been implicit in this discussion is time. The time required to find whether a suitable material exists is long enough; the time needed to develop a new material is considerably longer. The discovery in 1956–57 of ductility in single-crystal MgO has been followed, as indicated previously, by a very active program aimed at arriving at a ductile ceramic material. However, we are still many years away from actually having a usable material, and the applications requiring a ductile ceramic do not permit a waiting period. Material requirements may have to be reduced by the use of less extreme conditions, or substitute materials having other disadvantages may have to be used. Material composites such as sandwich structures or coated materials may have to be utilized for purposes which a truly flexible ceramic would serve alone.

Materials handling and processing is also important from the standpoint of hastening the application of new materials. Once a new material has been prepared (or new theoretical capabilities are proposed for a known material), the actual use of the material still must be developed. A good illustration of this factor occurs in the field of electronic materials. When a new semiconductor material is made, methods of purification must be found and proper doping agents, surface treatments, and means of attaching leads must be determined in order to achieve performance close to the potential capabilities of the material.

New Developments in Electronic Materials

The remarks above appropriately lead to a glance at some of the advances in electronics materials. Advances in solid state inorganic materials is the overlying topic of this discussion, and these materials have played an increasingly important role in the rapid rise of the electronic industry in the past decade. High-dielectric-constant materials such as barium titanate and the large family of magnetic ferrites were early examples of electronic materials. In addition, low-loss structural ceramics such as high aluminas and forsterites have found widespread use in the ceramic-metal electronic tube industry. Recent developments have taken place in each of these areas, but the most noteworthy developments have been in the area of semiconductor materials. All indications point to even greater advances in the latter field, with the market for semiconductor materials increasing manyfold in the next five years.

Much of the expansion in semiconductors will result from the continuing development of new devices and the discovery of frontier materials which offer great advantages over those now in use. Present electronic semiconductor devices such as transistors, diodes, tunnel diodes, and switches as well as miniaturized molecular circuits almost universally utilize single crystal wafers of ultra-high-purity germanium or silicon as their active elements. These materials have numerous disadvantages which have prevented the semiconductor devices from replacing vacuum tubes in many applications. Among these are low power, temperature limitations, upper frequency limitations, instability, noise, and poor resistance to radiation damage. Recently, in a search for better materials, attention has turned from the single-element semiconductors to certain compounds of two or more elements having improved properties in one or more of these areas. The most important new compounds for semiconductor purposes are those of the III–V and IV–IV groups.

Table 3 lists a few of the new compound semiconductors and compares their most important properties with those of the older semiconductors, silicon and germanium. Of particular note are their band gap and electron (and hole) mobilities. The larger the band gap, the higher is the temperature at which a semiconductor can be used as an active element.

Table 3. Comparison of Properties of Semiconductor Materials[a]

Semiconductor	Band gap (ev)	Electron mobility (cm^2/volt sec)	Melting point (°C)
Ge	0.7	3900	958
Si	1.1	1500	1414
SiC	2.8	>100	2700
C (diamond)	6.0–7.0	1800	>3500
InSb	0.18	65000	523
InP	1.25	>4000	1060
GaAs	1.35	>5000	1280

[a] JENNY, D. A., *Proceedings of the Institute of Radio Engineers*, 46, No. 6, 959 (1958).

Frequency response, on the other hand, depends on the carrier mobilities, with the highest response corresponding to the highest mobilities. An examination of the table will indicate that gallium arsenide and indium phosphide both have higher electron mobilities as well as wider band gaps than either silicon or germanium. Some gallium arsenide devices, including GaAs tunnel diodes, are already appearing on the market. This material, although rather scarce, offers good possibilities for improvement in both temperature performance and frequency response.

Because of its wide band gap, silicon carbide is also extremely promising for use as a high-temperature semiconductor. Application of this material has been hindered by the difficulty of growing silicon carbide crystals of sufficient size and (at the same time) of the required high purity, but progress is being made in this direction. As a semiconductor material, SiC has considerable theoretical interest because it is the only group IV–IV compound.

Table 3 indicates that if an inexpensive method were developed for producing high-purity single-crystal diamonds, these materials would also find application as superior high-temperature high-frequency semiconductors.

Indium antimonide is another material with great potential value for many applications. It has the highest electron mobility of any known semiconductor and therefore should have the highest frequency response. Its narrow band gap, however, requires that it be utilized below room temperature to take advantage of the desirable frequency response. Other important properties of indium antimonide are very high Hall and magnetoresistive coefficients (a change in resistivity of as much as 20 times is possible by the application of a magnetic field to this material) and high sensitivity to infrared radiation. Indium antimonide has important possibilities as a photoconductive

detector of infrared radiation. A unique property of this material is the variation in the limiting wavelength of response which can be produced by changing the impurity content.

Further advances in semiconductor materials are being made with ternary and multicomponent compounds as well as some of the rare earth compounds. By utilizing systems of continuous solid solution between two or more semiconductor compounds of different band gaps, a series of materials having continuous band-gap transitions can be obtained.

In the area of dielectric and magnetic materials, an interesting discovery is a series of materials which show both ferrimagnetic and ferroelectric properties. These materials consist of barium niobate plus a rare earth and iron oxide combined to form a single-phase structure. They not only are magnetic; they also have high dielectric constants. They may be useful for new components in which coupling between electric and magnetic effects is desirable. The temperature range over which both of these effects exist simultaneously can be adjusted by substituting different rare earth elements.

Research in the microwave field is continuing for improved materials for use at microwave frequencies, including materials for solid state Masers. ("Maser" is a coined term for "Microwave Amplification by Stimulated Emission of Radiation.") Conventional microwave amplifiers and oscillators convert dc energy into microwave energy by the interaction of electromagnetic radiation with moving electrons. In contrast, microwave Maser amplifiers and oscillators convert the internal energy of a molecular system into microwave energy by the interaction of radiation directly with the molecular system. Important materials for Maser applications include the yttrium and gadolinium iron garnets, ruby, and ruby doped with additional chromium.

Conclusion

A paraphrase of a recent declaration by a joint committee of the National Academy of Science and the National Research Council seems a fitting conclusion to this review of inorganic material advances. The committee declared that a "materials barrier" is holding up progress on defense, atomic energy, and space projects—that the properties of most presently available materials are inadequate for items which must withstand severe temperature, pressure, radiation, corrosion, and stress environments. Recommendations for removing this "barrier" include coordination of Government-sponsored materials development programs, incentives to encourage materials research, adequate stockpiles of important materials, and better dissemination of research information on new materials and their properties.

Harold E. Podall[1]
Ethyl Corporation
Baton Rouge, Louisiana

Recent Developments in Metal Carbonyl Synthesis

In recent years a number of important developments have occurred in the field of metal carbonyl chemistry. One of the key developments has been the discovery of the elusive manganese carbonyl; although the carbonyls of the neighboring metals, iron and chromium, have been known for a long time (see Table 1) it was not until 1954 that the characterization of manganese carbonyl was first reported (*2*). A number of other important publications then rapidly followed. First, a series of alkyl- and acylmanganese pentacarbonyls (*8*) were reported, these being the first examples of compounds containing a stable[2] sigma bond between carbon and a transition metal. Next were reported the most stable hydro-metal carbonyl known, hydromanganese pentacarbonyl, $HMn(CO)_5$ (*19*), and a number of very stable manganese carbonyl derivatives in which the effective atomic number of manganese is less than that of the next inert gas. The latter compounds, exemplified by triphenylphosphine manganese tetracarbonyl, $\phi_3PMn(CO)_4$, represent clean-cut examples of metal carbonyl derivatives which clearly violate the inert gas rule of Sidgwick and Bailey (*38*).

Recently another new metal carbonyl, vanadium carbonyl, has been reported (*26*, *37*). This will be discussed later in detail.

Aside from the discovery of these metal carbonyls, a number of important advances have been made relating to novel and improved syntheses for the various metal carbonyls. In this paper we should like to confine our attention primarily to the new synthetic methods. Before turning to a description of the methods it may be of interest to briefly review the historical background on the simple metal carbonyls (*1*, *23*).

[1] Present address, Melpar, Inc., Physical Sciences Laboratory, Falls Church, Virginia.

[2] The term stability as used in this paper refers to hydrolytic, air, and thermal stability at room temperature.

The known simple metal carbonyls and their originally published methods of preparation are listed in Table 1. The carbonyls of nickel, iron, cobalt, molybdenum, ruthenium, tungsten, and rhodium have been prepared by reaction of the finely divided metal with carbon monoxide at elevated temperature and pressure—the conversion of metal to carbonyl being very low in every case except for nickel and iron. The direct reaction between metal and carbon monoxide is thus of fairly specific synthetic value and will therefore not be further discussed.

Table 1. The Synthesis of Metal Carbonyls in Their Order of Publication

1890–1900	$Ni(CO)_4$[a], $Fe(CO)_5$[a] (Mond, *et al.*)
1900–1910	$Co_2(CO)_8$[a], $Mo(CO)_6$[a], $Ru(CO)_5$[a] (Mond, *et al.*)
1910–1920	.....
1920–1930	$Cr(CO)_6$[b] (Job, *et al.*); $W(CO)_6$[a] (I. G. Farbenindustrie)
1930–1940	.....
1940–1950	$Ir_2(CO)_8$[d], $Re_2(CO)_{10}$[c], $Os(CO)_5$[c], $Rh_2(CO)_8$[a]
1954	$Mn_2(CO)_{10}$[e] (Brimm, *et al.*)
1959	$V(CO)_6$[f] (Natta, *et al.*)

[a] From metal + CO.
[b] From $CrCl_3$ + $\phi MgBr$ + CO.
[c] From superoxide of metal + CO.
[d] From $IrCl_3$ + CO.
[e] From MnI_2 + Mg + CO.
[f] From VCl_3 + Mg-Zn + CO.

Group IV-B Carbonyls

The only carbonyl fully characterized in the literature for Group IV-B is bis-cyclopentadienyltitanium dicarbonyl, π-$Cy_2Ti(CO)_2$. It is a red-brown air-sensitive solid, mp 90° dec. It was reported by Murray (*24*) to have been prepared by reaction of bis-cyclopentadienyltitanium dichloride with two equivalents of sodium cyclopentadienide in benzene, followed by carbonylation of the intermediate *in situ* at 100° and 2000 psi of carbon monoxide for 8 hr.

Group V-B Carbonyls

The isolation and characterization of vanadium carbonyl was recently reported by Natta, *et al.* (*26*), and shortly thereafter by Pruett and Wyman (*37*). Natta, *et al.* (*26*), reported it as being a very volatile green-black solid which decomposes at 60–70° under nitrogen. The compound was found to be paramagnetic in the solid state with one unpaired electron, and appeared to be the monomeric hexacarbonyl according to elemental and single crystal X-ray analyses. Moreover, the X-ray analysis indicated that it possesses the same structure as the Group VI-B metal carbonyls, i.e., octahedral arrangement of the CO ligands about the central metal atom. Pruett and Wyman then reported the synthesis of vanadium hexacarbonyl by reacting bis π-toluene vanadium with carbon monoxide. These workers originally assigned this compound a dimeric formula, $[V(CO)_6]_2$ based upon cryoscopic molecular weight and magnetic measurements in benzene. Since then it has been found by Calderazzo, *et al.* (*6*, *7*), that the cryoscopic method may lead to erroneous conclusions regarding the molecular weight of metal carbonyls. In addition they have found that vanadium hexacarbonyl in solution is also paramagnetic with one unpaired electron. Accordingly, it appears fairly certain now that vanadium hexacarbonyl is monomeric.

Ercoli, *et al.* (*13*), prepared vanadium carbonyl in 40–50% yields by the reductive-carbonylation method (*32*) involving reaction of vanadium trichloride with magnesium-zinc couple, activated with iodine, and carbon monoxide in pyridine at 135° and 3000 psi. Recently, Werner and Podall (*39*) prepared this carbonyl in quantitative yield by treatment of bis-diglyme[3]-sodium hexacarbonylvanadate (−1) with 100% phosphoric acid at 25° followed by vacuum sublimation at about 45–50°. The bis-diglyme complexes of vanadium, niobium, and tantalum (*39*) were prepared by reductively carbonylating the metal chlorides, VCl_3, $NbCl_5$, and $TaCl_5$, with excess sodium and carbon monoxide in diglyme, as exemplified for vanadium as follows:

$$VCl_3 + 6Na + 6CO \xrightarrow[\text{diglyme}]{\substack{100° \\ 300\ \text{psi}}} (\text{diglyme})_2Na^+V(CO)_6^- \qquad 80\%\ \text{yield}$$

The complexes involving niobium and tantalum represent the first known carbonyls of these metals. They are yellow solids, mp 173–176° dec, in the case of the vanadium and tantalum compounds, which decompose slowly in air and light but are considerably more stable than vanadium hexacarbonyl. The greater stability is evidently due to the fact that the complexes involve inert gas structures.

Group VI-B Carbonyls

The first preparation of chromium carbonyl, by Job and Cassal (*22*) in 1923, was by the Grignard method. Until recently this constituted the only preparative method available for this compound. The yield of chromium carbonyl by various modifications of this method as developed by Job and Rouvillois (*22*), Hieber and Romberg (*18*), and by Nesmeyanov and Anisimov (*27*) was at best only about 20%. In 1947 Owen, English, Cassidy, and Dundon (*31*) markedly improved the yield to 67%. The improvement was brought about by employing high mole ratios of Grignard reagent to chromic chloride and by contacting the reactants at low temperatures, about −70°, prior to carbonylation. In order to obtain the metal carbonyl by this method it is necessary to hydrolyze the reaction mixture, since the carbonyl itself is not present as such before hydrolysis. The method appears to be suitable only for the group VI-B metal halides where the oxidation state of Cr is +3, Mo is +5, and W is +6. The halides of these metals in lower oxidation states are reportedly unsatisfactory (*21*, *22*, *31*). For further details on this method the reader is referred to the excellent review article by Cumming, *et al.* (*11*).

In 1955 Brimm, *et al.* (*3*), reported the preparation of chromium carbonyl in 69% yield by the reaction:

$$CrCl_3 + 5.5\ Mg + 0.52\ I_2 \xrightarrow[\substack{2200\ \text{psi CO} \\ \text{in } Et_2O}]{40°/8\ \text{hr}} Cr(CO)_6$$

[3] Diglyme = dimethyl ether of diethylene glycol.

The authors specified that at least 1 mole of iodine was required for every 5 moles of chromic chloride, and that the function of the iodine was to convert the chloride (presumably via magnesium iodide) to the more soluble and hence more reactive chromic iodide. Although finely divided zinc, iron, and aluminum have been used successfully for the preparation of the other Group VI-B metal carbonyls, such as molybdenum and tungsten carbonyl, this method had not been suitable for chromium carbonyl.[4] Shortly thereafter, Natta, *et al.* (*25*), reported essentially the same method with two modifications: use of the soluble chromic acetylacetonate in place of chromic chloride, and use of pyridine as the preferred solvent. In this case an 82% yield of chromium carbonyl was reported.

An interesting feature of this method is that the metal carbonyl is reportedly produced directly as such and therefore does not require hydrolysis in order to liberate it. These workers attributed the success of the method as being due to the formation of pyridine complexes as intermediates which facilitate the over-all reaction. Evidence for this, however, was not presented. A similar method employing lithium, sodium, or magnesium in pyridine has more recently been reported by Nesmeyanov, *et al.* (*29*). In the best case, a 37% yield of chromium carbonyl was obtained employing a 4:1 mole ratio of sodium to chromic chloride in pyridine under 3700 psi of carbon monoxide at 22° for about 5 hr. Yields of 80% or better have been obtained for chromium, molybdenum, and tungsten carbonyl by Podall, *et al.* (*35*), by reductively carbonylating the metal chloride with sodium and carbon monoxide at −10–25° in diglyme followed by hydrolytic carbonylation at 0°. The reaction sequence as exemplified for the synthesis of chromium carbonyl is as follows:

$$CrCl_3 + 5Na + 5CO \xrightarrow[\substack{800\text{ psi}\\ \text{diglyme}\\ \text{solvent}}]{-10\text{–}25^\circ} 2[(\text{diglyme})_2Na]^+Cr(CO)_5^- \quad \text{(I)}$$

$$\text{(I)} + H_3O^+ + CO \xrightarrow[800\text{ psi}]{0^\circ} Cr(CO)_6$$

The latter step is conducted by adding aqueous sulfuric acid slowly to (I) *in situ* under 800 psi of carbon monoxide. It is interesting to note that in this case the metal carbonyl is produced initially as a sodium salt complex with diglyme while with Natta's method (*25*), which employs pyridine as solvent, the metal carbonyl is reportedly produced directly as such. The difference may be due to the greater reducing power of sodium compared with magnesium with respect to chromium carbonyl in the formation of metal salt complexes and also to the greater coordinating power of diglyme compared with pyridine in stabilizing the sodium salt.

In 1957 Fischer and Hafner (*15*) reported the preparation of chromium carbonyl in 83% yield by the reaction:

$$CrCl_3 + 5.8\ Al + 0.6\ AlCl_3 \xrightarrow[\substack{2500\text{ psi CO}\\ \text{in benzene}}]{140^\circ/14\text{ hr}} Cr(CO)_6$$

[4] See reference *18*. These workers attempted to use zinc as the reducing agent in alcohol as well as in water, without success.

More recently (*16*) these workers have reported yields up to 90% by use of equimolar quantities of $AlCl_3$ to $CrCl_3$ under otherwise comparable conditions employing stainless steel balls to achieve more intimate contact of the reactants in the rocking autoclave.

In 1958 Zakharkin, *et al.* (*40*), and shortly thereafter Podall (*32*) reported the preparation of the Group VI-B metal carbonyls, viz. chromium, molybdenum, and tungsten carbonyl, by the use of alkylaluminum compounds such as triethylaluminum or di-isobutylaluminum hydride as reducing agents. The method consists of reacting an appropriate chloride of the metal with the alkylaluminum compound and carbon monoxide. Yields of 90% or better have been obtained under certain conditions (*33*). Thus, reaction of chromic chloride with triethylaluminum at a 1:6 mole ratio and 1000 psi of carbon monoxide in diethyl ether at 115° for 7 hr. provides chromium carbonyl in 92% yield.

Nesmeyanov, *et al.* (*30*), reported the preparation of molybdenum and tungsten carbonyl by a novel method involving the use of iron pentacarbonyl as a simultaneous reducing and carbonylating reagent. In the case of tungsten carbonyl, 72–75% yields were obtained when employing a 3:1 mole ratio of $Fe(CO)_5$ to WCl_6 at 90° in diethyl ether. The yield was improved to 85% when the reaction was conducted under 900 psi of hydrogen at 70°. In the case of molybdenum carbonyl, the highest yield (29%) was obtained at a 2.5:1 mole ratio of $Fe(CO)_5$ to $MoCl_5$ in the presence of one mole of HCl per mole of $MoCl_5$ at 190° in diethyl ether. No mention was made of the applicability of this method to the synthesis of chromium carbonyl.

In continuation of their studies of different reducing agents for the preparation of Group VI-B metal carbonyls, Nesmeyanov, *et al.* (*28*), found that lithium aluminum hydride may be employed for the preparation of chromium carbonyl in 65% yield.

$$CrCl_3 + 3\ LiAlH_4 + 6\ CO \xrightarrow[\substack{1500\text{ psi CO}\\ \text{in } Et_2O}]{65^\circ} Cr(CO)_6$$

Group VII-B Carbonyls

In 1949 Hurd, *et al.* (*21*), reported evidence for the formation of certain manganese carbonyl fragments via the Grignard method, wherein manganese iodide was contacted with an excess of the phenyl Grignard reagent and carbon monoxide according to the procedure of Owen, *et al.* (*31*). The isolation and characterization of manganese carbonyl was first reported by Brimm, *et al.* (*2*), in 1954. The method consisted of reacting a specially prepared form of manganese iodide with magnesium powder and 3000 psi of carbon monoxide in diethyl ether at 25° in a ball mill.

$$Mn + 2\ CuI \xrightarrow{500^\circ} [MnI_2 + 2\ Cu]$$

$$MnI_2 + 2\ Cu + 2\ Mg \xrightarrow[\substack{3000\text{ psi CO}\\ \text{in } Et_2O}]{25^\circ/16\text{ hr}} [Mn(CO)_5]_2 \quad (1\%\text{ yield})$$

Manganese chloride and bromide, prepared by the cuprous halide method, were found to be ineffective

in this reaction, as was manganese iodide prepared from the elements. A number of other variables, such as temperature, pressure, and solvent, were also investigated without avail in an effort to improve the yield. These investigations established the formula of manganese carbonyl as being dimeric and suggested on the basis of its infrared spectrum that the molecule contains a simple Mn—Mn bond with no CO bridging. Since then Rundle, *et al.* (*12*), have investigated the structure of manganese carbonyl in greater detail via X-ray diffraction and have concluded that it contains a long Mn—Mn bond with the CO ligands octahedrally disposed about each manganese atom. These workers also investigated the X-ray diffraction pattern of rhenium carbonyl, $[Re(CO)_5]_2$, and concluded that its structure was similar to that of manganese carbonyl.

In 1958, Closson, *et al.* (*8*), reported the preparation of manganese carbonyl in 32% yield by a novel and superior method, the sodium-benzophenone method. This procedure consists of forming the manganese ketyl of benzophenone by reaction of manganese chloride with two equivalents of the sodium ketyl in tetrahydrofuran, followed by carbonylation at 165°, 2000 psi of carbon monoxide, hydrolysis, and then steam distillation of the product. This represented the first satisfactory method developed for the preparation of manganese carbonyl in appreciable quantity, and facilitated the subsequent investigation of its interesting chemistry (*9*). It might be noted that the sodium-benzophenone method can also be used for the preparation of chromium carbonyl and provides it readily in about 65% yield.

Manganese carbonyl is a yellow solid, mp 155°, which can be isolated and handled in the presence of air and light, in which it is moderately stable. It is soluble in ethers and hydrocarbons, can be sublimed *in vacuo*, and starts to decompose at about 160° under nitrogen.

Before moving on to the most recent methods, it is of interest that the Grignard method itself has been improved by Hnizda (*20*) to provide manganese carbonyl in 9% yield. The improvement was brought about by contacting finely divided manganese chloride with excess phenyl Grignard and 2000 psi of carbon monoxide in diethyl ether at −15°.

In 1959, Podall and Shapiro (*34*) reported the applicability of the alkylaluminum method to the preparation of manganese carbonyl. In this case the method consists of reacting a suitable salt of manganese, such as the acetate, with an alkylaluminum compound, such as triethylaluminum, and carbon monoxide in an appropriate solvent (generally an ether), or under appropriate contact conditions when a coordinating solvent is not employed, at elevated temperature and pressure. Manganese carbonyl can thus be prepared in 55–60% yield by reacting manganese acetate with triethylaluminum, at a 1:4 mole ratio, and 3000 psi of carbon monoxide in isopropyl ether at 100° for 5 hours (*33*, *34*).

The alkylaluminum procedure differs from the Grignard method in that little or none of the free transition metal is produced as side product, hydrolysis of the reaction mixture is not required in order to liberate the metal carbonyl, and the halides of the transition metals in lower oxidation state also work in this reaction (*32*, *33*). Thus, although chromous chloride is essentially ineffective in the Grignard method, it works satisfactorily in the alkylaluminum method. The differences between the two methods can for the most part be explained in terms of the lower reactivity and hence the greater selectivity of an alkylaluminum compound compared to a Grignard reagent in their reactions with a transition metal salt. The reaction has therefore been given the name "reductive carbonylation" (*32*) to signify the importance of synchronizing the rate of carbonylation with the rate of reduction in order to obtain a high yield of the metal carbonyl.

In studying the applicability of the reductive carbonylation reaction for the synthesis of various known and novel metal carbonyls utilizing various reducing agents, Podall, *et al.* (*36*), have recently prepared manganese carbonyl in 45–50% yields by reacting π-methylcyclopentadienylmanganese tricarbonyl with excess sodium and carbon monoxide in diglyme at 125° and 700 psi pressure. An interesting feature of this route is the marked effect of diglyme upon the yield. In benzene a temperature of about 200° was required to effect carbonylation and the yield of manganese carbonyl was only 15%.

Summary and Conclusion

The various preparative methods for chromium, manganese, and vanadium carbonyl, together with the respective yields, are summarized in Table 2. These and the other methods for all of the known metal carbonyls may be classified in terms of the following four basic reaction types.

Direct Addition Reaction

$$M + CO \rightarrow M{-}CO$$

Examples: $Ni + 4\ CO \rightarrow Ni(CO)_4$

Displacement or Abstraction Reaction

$$MX + 2\ CO \rightarrow M{-}CO + X{-}CO$$

Example: $2\ IrCl_3 + 11\ CO \rightarrow Ir_2(CO)_8 + 3\ COCl_2$

$$Re_2O_7 + 17\ CO \rightarrow Re_2(CO)_{10} + 7\ CO_2$$

$$\text{M-ketyl} + CO \rightarrow M{-}CO + \text{ketone}$$

Example: $2\ Mn(OC\phi_2)_2 + 10\ CO \rightarrow Mn_2(CO)_{10} + 4\ \phi_2CO$

Reductive Carbonylation Reaction

$$MX + R + CO \rightarrow M{-}CO + RX$$

In this method R may be (*a*) an organometallic reagent, such as ϕMgBr or Et_3Al, which serves to form a metastable intermediate of the transition metal, M; (*b*) a metal reducing agent, preferably in the presence of another reagent which serves to stabilize a lower oxidation state of M for carbonylation, e.g. the Al-$AlCl_3$ couple; or (*c*) an inorganic reducing agent, such as sodium hyposulfite, $Na_2S_2O_4$, used for the synthesis of $Co_2(CO)_8$ (*17*).

Exchange Reaction

$$MX + Fe(CO)_5 \rightarrow M{-}CO + FeX$$

Insufficient information is available at this time concerning the nature of the reaction to warrant a specific classification within the other methods. According to Nesmeyanov, *et al.* (*30*), a metal halide, such as $MoCl_5$ or WCl_6, reacts directly with $Fe(CO)_5$ at room temperature to form a product which may be the intermediate required for metal carbonyl formation. They did not define the nature of this product.

Of the various methods developed for the preparation of the relatively inaccessible chromium, manganese, and vanadium carbonyls, it is evident from Table 2

that the reductive carbonylation method has met with the greatest use. It is apparent that this method is of considerable scope and may be capable of yet further extension to the synthesis of other novel metal carbonyls. It is rather interesting that although this method was only relatively recently defined and elaborated (*32*, *33*, *35*), it was actually employed long ago, though under no specific name, by Manchot, Hieber,

Table 2. Summary of Preparative Methods for Chromium, Manganese, and Vanadium Carbonyl

Method	% Yield of metal carbonyl[a] Cr	Mn	V
Grignard	67	9	...
Mg–I_2	69	1	...
Mg-I_2-py	82[b]	...	...
MgZn-I_2-py	...	...	45
Na-py	37	...	...
Na-diglyme	80	45[c]	80
Al-$AlCl_3$	90	...	...
Et_3Al	92	55	...
Na-ϕ_2CO	65	32	...

[a] Based on metal salt.
[b] Uses chromic acetylacetonate, py denotes pyridine.
[c] Uses π-methylcyclopentadienylmanganese tricarbonyl as source of manganese.

and others for the preparation of various metal carbonyls. Thus, a typical procedure consisted of contacting the metal halide of interest with carbon monoxide in the presence of a "halogen accepter" such as copper or silver. In conclusion, such successful renovation of a synthetic method serves to illustrate that very fruitful results in synthesis can sometimes be achieved by reconsidering a given synthesis reaction in terms of its broadest mechanistic features.

Acknowledgment

The author wishes to thank Dr. H. Sternberg of the Bureau of Mines and Dr. H. H. Jaffe of the University of Cincinnati for suggesting the publication of the original paper presented at the Organometallic Symposium of the Southwest Regional Meeting of the ACS, Baton Rouge, Louisiana, December, 1959, and Dr. J. D. Johnston for his helpful suggestions regarding the preparation of the original manuscript.

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W. Manch and
W. Conard Fernelius
The Pennsylvania State University
University Park

The Structure and Spectra of Nickel(II) and Copper(II) Complexes

Many important features of the chemistry of nickel and copper complexes cannot be explained in terms of the valence bond theory. According to valence bond theory the structure and bonding involved in a nickel complex are described by one parameter, the magnetic moment (*27*). (The color of a complex is often used as an alternate (*20*) because of its apparent connection with the magnetic moment). Using the magnetic moment (or color) of a complex as a guide, structures are then assigned on the basis of the orbitals available for hybridization. Thus, paramagnetic 4-coordinate nickel complexes are considered to be tetrahedral and ionic while diamagnetic 4-coordinate complexes are square planar and covalent.

However, these simple generalizations are not adequate. For example, how is one to describe the structure and bonding of a complex which has an intermediate magnetic moment (*33*), i.e., one whose value is somewhere between diamagnetic and that due to two unpaired electrons, 2.8 Bohr magnetons? In addition, some complexes are known which can be prepared in both a diamagnetic and a paramagnetic form (*2*). How can the valence bond theory be applied to complexes such as these?

The variable coordination number of nickel creates another problem which is difficult for the valence bond theory to accommodate. Complexes of penta- and hexa-coordinate nickel can be described only with the use of outer (4*d*) orbitals in the hybridization (*21*). This is also the most common explanation given to complexes of copper. Because of energy differences the suitability of using such orbitals is open to question.

The use of the valence bond theory is often justified by its simplicity. It provides a picture of bonding sufficient for treating many chemical problems. However, it is the purpose of this paper to discuss an equally simple theory based on the ionic bond and the simple fact that like charges repel each other. In terms of this, the *crystal field theory*, there need not be a connection between the magnetic moment and structure. This theory also leads to a more meaningful connection between the spectrum of a complex and its structure.

In the last ten years the application of the crystal field theory to bonding has contributed significantly to the understanding of the chemistry of coordination compounds. This theory, developed by Bethe (*5*), was applied to general problems of the chemistry of complexes by Orgel (*23*) in 1952. Since that time, its application has yielded many important results. One of its major accomplishments, the interpretations of the visible absorption spectra of nickel and copper complexes, will be dealt with in this communication. However, before considering the spectra of complexes, a brief discussion[1] of the essential features of the theory is appropriate.

The Crystal Field Theory

The crystal field theory is based on electrostatic theory in which the bonding is considered to be purely electrostatic. It is actually a correction to the electrostatic theory which amounts to a consideration of the interaction between the electrostatic field of the ligands and the *d* electrons of a metal ion.

To illustrate this interaction, it is first necessary to describe the *d* orbitals. This may be done most simply by means of Figure 1 (*29*),[2] in which the angular distribution portion of the wave functions for the *d* electrons are shown.

Consider now the effect of placing six ligands around a metal ion. With the ligands in an octahedral arrangement, two of the orbitals, the $d_{x^2-y^2}$ and d_{z^2}, will be in direct line with them (Fig. 2). The remaining orbitals, the d_{xz}, d_{xy}, and d_{yz}, are oriented (Fig. 1) so that each lobe is directed toward a point mid-way between any two ligands. From these figures it can be seen that, because of the electrostatic field of the ligands, the potential energy of an electron in the $d_{x^2-y^2}$ or the d_{z^2} orbitals will be higher than that of an electron in either the d_{xy}, d_{xz}, or d_{yz} orbitals. Since an electron will seek the position of lowest potential energy, a preferential filling of the *d* orbitals will occur. Thus, the first three electrons would occupy the low energy d_{xy}, d_{xz}, or d_{yz} orbitals. The orbital taken by the fourth electron will depend on the nature of the ligands. If the electrostatic field of a ligand is slight, as it is for H_2O, the energy required to pair the fourth electron with one already present (in any of the d_{xy}, d_{xz}, or d_{yz} orbitals) will be more than the exchange *interaction energy* of the electrons with parallel spins (*25*, *31*), so pairing will not occur. The electron will then enter either the $d_{x^2-y^2}$ or the d_{z^2} orbital. If the field is strong, as it is for cyanide ion, the energy required to pair the

The authors are indebted to the Atomic Energy Commission for the financial support which made this review possible. During its preparation W. Manch served as a Research Assistant under Contract Number AT (30-1)-907.

Present addresses are W. Manch, The University of Copenhagen, Denmark; and W. C. Fernelius, Koppers Co., Inc., Pittsburgh 19, Pa.

[1] For further information concerning this theory see references *3*, *7*, *9*, *22*, *25*, *26*, *29*, *30*, and *31*.

[2] These figures (reproduced from reference *29*) are obtained by plotting the angular portion of the wave function for a *d* electron. The radial portion of the wave function has been neglected in these plots.

The symbols d_{xy}, d_{xz}, etc., are arbitrary labels depending upon the placement of the cartesian coordinates. For the d_{xy}, d_{yz}, and d_{xy} the label indicates the plane in which the orbital is situated. The $d_{x^2-y^2}$ and d_{z^2} then are on the axes.

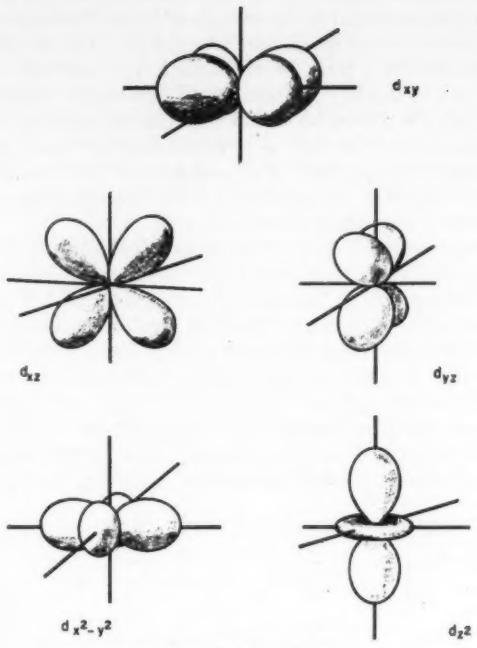


Figure 1. The angular distribution of the *d* orbitals.

fourth electron will be less than the exchange interaction energy so pairing will occur.

Figure 2. Electrostatic interaction of six ligands with the $d_{x^2-y^2}$ and the d_{z^2} orbitals.

Using this model, we see that for an octahedral arrangement of ligands three of the *d* orbitals are of equally low energy while two are of equally high energy. This is illustrated schematically in Figure 3, in which the energy of the *d* orbitals of the gaseous ion (*a*),[3] the energy of the *d* orbitals of the complexed metal ion before splitting occurs (*b*), and the relative energies of the split *d* orbitals are shown.

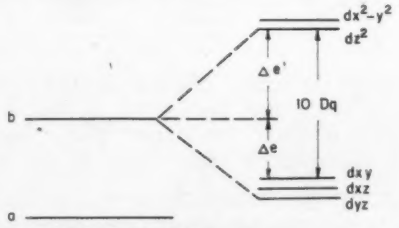


Figure 3. Octahedral energy level diagram.

In Figure 3, 10 *Dq*, representing the total energy separation, may be divided into two portions, Δe and $\Delta e'$: Δe represents the energy lost (i.e., stabilization) by the system for each electron occupying the low energy level, and $\Delta e'$ represents the energy gained by the system for each electron occupying the high energy level. The amount of energy lost and gained must be equal if the *d* orbitals are completely occupied. Since the low energy level can contain six electrons, and the high energy level can contain four, it follows that

$$\Delta e \neq \Delta e'$$

but
$$6\Delta e = 4\Delta e'.$$

Since
$$\Delta e + \Delta e' = 10\ Dq$$

then
$$\Delta e' = 6\ Dq \text{ and } \Delta e = 4\ Dq.$$

These values represent the relative stabilities of the *d* orbitals in an octahedral complex only. For a different symmetry a new set must be derived from the appropriate energy level diagram. Figure 4 represents

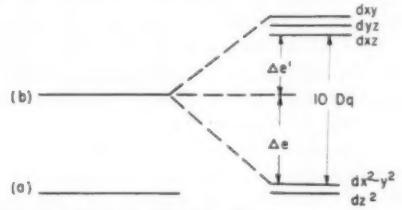


Figure 4. Tetrahedral energy level diagram.

the energy-level diagram for a tetrahedral symmetry and Table I gives the values of Δe and $\Delta e'$ for the octahedral and tetrahedral arrangement of ligands.

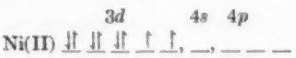
Table 1. Δe (−) and $\Delta e'$ (+) in Terms of *Dq*

Symmetry	d_{z^2}	$d_{x^2-y^2}$	d_{xy}	d_{xz}	d_{yz}
Tetrahedral	−6.0	−6.0	+4.0	+4.0	+4.0
Octahedral	+6.0	6.0	−4.0	−4.0	−4.0

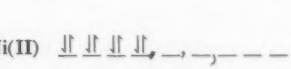
With this introduction to crystal field theory, it is now possible to proceed with its application to the complexes of nickel and copper. In the next section, the relative stabilities of the various stereochemistries of nickel complexes will be considered followed by a discussion of the spectra observed for the different symmetries. Then we will deal with the structure and spectra of copper complexes, and in the final section the significance of the symmetry symbols used throughout the paper will be explained.

The Stereochemistry of Nickel Complexes

The electronic structure of nickel(II) may be represented as:



or



In view of the orbitals available for hybridization the valence bond theory predicts two possible stereochemistries for tetracoordinate nickel complexes. The diamagnetic or spin-paired complexes will be square planar (dsp^2) while paramagnetic or spin-free complexes

[3] It should be understood that in the absence of a crystal field the energies of all five *d* orbitals are the same.

will be tetrahedral (sp^3). Using this theory the structure of a complex was frequently inferred from its magnetic moment. However, the recently developed crystal field theory challenges the supposition that there is a connection between the magnetic properties and the structure of a complex.

According to the crystal field theory the tetrahedral arrangement of ligands around a paramagnetic nickel ion is the least preferred. Instead, the octahedral structure is preferred because the crystal field stabilization energy is larger for this symmetry. Calculation of the stabilization energy is simple and may be illustrated with Table 1 and Figures 3 and 4.

In the octahedral symmetry, the eight d electrons of the nickel ion are distributed unequally between the high and low energy levels. There are six electrons in the low energy (d_{xy}, d_{xz}, d_{yz}) levels while two electrons occupy the high energy ($d_{x^2-y^2}$, d_{z^2}) levels. In Table 1 we find the energy change (Δe), when one electron enters the low energy level to be $-4Dq$, while that for six electrons is $-24Dq$. The energy change ($\Delta e'$), when an electron enters the high energy level is $+6Dq$, and that for two electrons is $+12Dq$. The difference, $-12Dq$, is the crystal field stabilization energy. The system is $12Dq$ more stable than it would be if the d orbitals had not split in energy.

In the tetrahedral symmetry the eight d electrons are distributed equally between the high and low energy levels. Using the relative stabilities, Δe and $\Delta e'$, in Table 1 we find that the stabilization energy for this symmetry is -8 Dq. Thus, even if Dq is equal in both symmetries (which as we shall see, it is not) the tetrahedral structure is less preferred.

Visible Absorption Spectra of Nickel Complexes

In 1951, Hartman and Ilse (*13*) used the crystal field theory to explain the old problem of the origin of visible absorption spectra. They found that an absorption band is due to the transition of an electron from one d orbital to another. Such a transition is possible because the energies of the d orbitals have been split by the electrostatic field of the ligands. If the ligands are assumed to be point charges or dipoles, the transition energies in terms of the amount of splitting (10 Dq) may be calculated by means of the quantum mechanical perturbation theory. A summary of the general methods of calculation may be found in ref. 7. A few of the results obtained will be presented here to illustrate the application of the calculations.

An early example is Ballhausen's (*1*) treatment of the spectra of nickel complexes. In this work Ballhausen calculated the frequency of the absorption bands in the spectra of the compounds listed in Table 2.[4] The observed spectra are also listed.

Ballhausen generalizes the results of the calculations by means of the following equations.

$$\nu_1 = 10Dq$$

$$\nu_3 = 9/5\ (10Dq)$$

$$\nu_4 = 17{,}000 + 6/5\ (10Dq)$$

where ν is the frequency of the absorption band in cm^{-1} and is proportional to the energy difference between the two levels involved in the transition. To use these equations $10Dq$ may be calculated[5] by quantum mechanical methods. To test for an octahedral complex, the only symmetry to which the equations apply, only the position of the first absorption must be taken from the observed spectra. The positions of the remaining bands may then be calculated from the equations and compared with those observed.

From the equations, the ratio ν_3/ν_1 is found to be 1.8 for octahedral nickel complexes. This ratio is one of the distinguishing features of octahedral nickel complexes and is included in the data given for other nickel complexes discussed in a later section (see Table 3).

If the energies of the various levels derived from equations similar to those given above are plotted against $10Dq$, an energy level diagram, now called an Orgel Diagram (*24*), is obtained. The Orgel diagram for octahedral nickel complexes is given in Figure

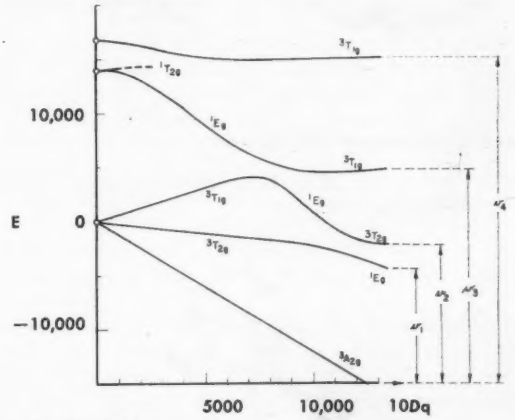


Figure 5. Orgel diagram.

5.[6,7] Jørgensen (*16*) has shown that Figure 5 is applicable to any complex, whatever the ligands, as long as the average environment about the nickel ion is approximately the same. (See the variety of complexes in Table 3, which have been fitted to this diagram.)

A similar diagram for square planar complexes has been published by Maki (*17*). In this diagram

Table 2. A Comparison of Calculated and Observed Absorption Spectra

	$Ni(H_2O)_6^{++}$		$Ni(en)_3^{++}$	
	Observed	Calculated	Observed	Calculated
ν_1	8,000 cm^{-1}	7,600 cm^{-1}	11,200 cm^{-1}	10,500 cm^{-1}
ν_3	14,000	13,700	18,300	18,900
ν_4	25,300	26,000	29,000	29,500
ν_3/ν_1	1.75	1.80	1.64	1.8

[4] The absorption bands ν_2 and ν_4 given here were originally assigned as ν_2 and ν_3 by Ballhausen. These bands (representing the two transitions $^3A_{1g} \rightarrow {}^3T_{1g}$) have since been shown to be ν_3 and ν_4 for most complexes and are so labeled throughout the text.

[5] Dq can be calculated, but only with great difficulty and poor results.

[6] This diagram is not that orginally published by Orgel. This one is a modification of the original and was developed by Jørgensen(*15*). Jørgensen's symbolism has been changed in order to be consistent with that used throughout this paper.

[7] The symbols $^3A_{2g}$, etc. represent the symmetry of the state to which they are assigned. The procedure for obtaining these symbols will be described in the last section.

(Fig. 6) the effective dipole moment of the ligand (μ) replaces the parameter, Dq. The diagram is also limited to certain values of R, the approximate metal-ligand bond distance. These parameters are necessitated by the lower symmetry of square planar complexes. Because of the dependence of the energy level diagram on these parameters Figure 6 is not applicable to all square planar complexes. It is specific for complexes in which all four coordinating atoms are the same. For complexes in which two different pairs of atoms are coordinated, one of two other diagrams, depending upon the geometrical arrangement of the coordinated atoms (e.g., *cis* or *trans*) must be used. The essential features of all these diagrams are nearly the same. Their application to the spectra of the complexes is the same as that to be illustrated in a later section with Figure 6. Thus the diagrams will not be given here but are in the papers by Maki.

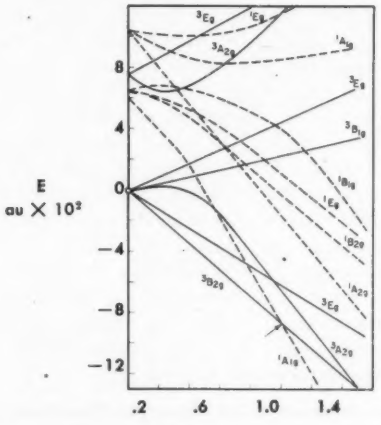


Figure 6. State energies in four coordinate complexes. au = atomic units. 1 au = 2.187 × 10^5cm^{-1}. μ is also in atomic units. 1 au = 2.54D.

The Visible Absorption Spectra of Octahedral Complexes

On the basis of the simple energy level diagram in Figure 3 only one absorption band is expected for octahedral complexes. However, Figure 5 shows that the d orbital energies are much more complicated because electronic interactions tend to split the orbitals beyond that shown in Figure 3. Thus, instead of one band most octahedral nickel complexes show at least four.

The spectra of a large number of octahedral nickel complexes have been determined by Jorgensen (*16*). Some examples are listed in Table 3. Besides the band position, the table includes the intensity of the band, expressed as the extinction coefficient, and the assignment of the band in terms of the symbols representing the various energy states. Values for the ratio ν_3/ν_1 have been included with these data.

These spectra have several distinguishing features. First, the wavelength of absorption is characteristic. There are generally four bands in the ranges 8000–11,000; 12,000–13,000; 15,000–19,000; 25,000–29,000 cm^{-1}. In addition, the extinction coefficients of the bands are small (of the order of 1–30) and the ratio ν_3/ν_1 is 1.6–1.8.

Table 3. The Spectra of Octahedral Nickel Complexes

Compound	Transition	λ (mμ)	ν (cm^{-1})	Intensity	ν_3/ν_1
Ni(enta)$^=$	$^3A_{2g} \rightarrow {}^3T_{2g}$	990	10,100	3.1	...
	$^3A_{2g} \rightarrow {}^1E_g$	788	12,700	5.4	1.68
	$^3A_{2g} \rightarrow {}^3T_{1g}$	588	17,000	8.4	...
	$^3A_{2g} \rightarrow {}^3T_{1g}$	382	26,200	12.6	...
Ni(enta)$NH_3^=$	$^3A_{2g} \rightarrow {}^3T_{2g}$	980	10,200	16.6	...
	$^3A_{2g} \rightarrow {}^1E_g$	788	12,700	3.4	1.69
	$^3A_{2g} \rightarrow {}^3T_{1g}$	582	17,200	10.9	...
	$^3A_{2g} \rightarrow {}^3T_{1g}$	372	26,900	20.2	...
Ni(enta)en$^=$	$^3A_{2g} \rightarrow {}^3T_{2g}$	995	10,050	25.0	...
	$^3A_{2g} \rightarrow {}^1E_g$	800	12,550	4.7	1.68
	$^3A_{2g} \rightarrow {}^3T_{1g}$	579	17,300	8.1	...
	$^3A_{2g} \rightarrow {}^3T_{1g}$	369	27,100	10.8	...
Ni(tetren)NH_3	$^3A_{2g} \rightarrow {}^3T_{2g}$	900	11,100	13.0	...
	$^3A_{2g} \rightarrow {}^1E_g$	800	12,500	9.0	1.69
	$^3A_{2g} \rightarrow {}^3T_{1g}$	535	18,700	8.3	...
	$^3A_{2g} \rightarrow {}^3T_{1g}$	350	28,600	11.0	...
Ni(bdn)$_3^{++}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	915	10,950	...	...
	$^3A_{2g} \rightarrow {}^1E_g$	788	12,700	...	1.64
	$^3A_{2g} \rightarrow {}^3T_{1g}$	556	18,000	...	...
	$^3A_{2g} \rightarrow {}^3T_{1g}$	350	28,600	...	...
Ni$(H_2O)_6^{++}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	1175	8,500	2.0	...
	$^3A_{2g} \rightarrow {}^1E_g$	740	13,500	1.8	1.81
	$^3A_{2g} \rightarrow {}^3T_{1g}$	650	15,400	1.5	...
	$^3A_{2g} \rightarrow {}^3T_{1g}$	396	25,300	5.2	...
Ni$(NH_3)_6^{++}$	$^3A_{2g} \rightarrow {}^3T_{2g}$	930	10,750	4.0	...
	$^3A_{2g} \rightarrow {}^1E_g$	760	13,150	5.0	1.63
	$^3A_{2g} \rightarrow {}^3T_{1g}$	572	17,500	4.8	...
	$^3A_{2g} \rightarrow {}^3T_{1g}$	355	28,200	6.3	...
Ni(en)$_3^{++}$	$^3A_{1g} \rightarrow {}^3T_{2g}$	894	11,200	7.3	...
	$^3A_{1g} \rightarrow {}^1E_g$	807	12,400	5	1.65
	$^3A_{1g} \rightarrow {}^3T_{1g}$	545	18,350	6.7	...
	$^3A_{1g} \rightarrow {}^3T_{1g}$	345	29,000	8.6	...

All spectra are for water solutions. Enta = ethylenediaminetetraacetate; en = ethylenediamine; tetren = tetraethylenepentamine; bdn = 1,3-diaminobutane.

The Visible Absorption Spectra of Square Planar Complexes

The spectra of some typical square planar complexes, along with extinction coefficients and transition assignments are listed in Table 4 (*18*).

Table 4. The Spectra of Square Planar Complexes

Compound	Transition	λ (mμ)	ν (cm^{-1})	Intensity
Ni(DMG)$_2$	$^1A_{1g} \rightarrow {}^1A_{2g}$	475	21,100	120
	$^1A_{1g} \rightarrow {}^1B_{2g}$	410	24,400	520
Ni(DϕG)$_2$	$^1A_{1g} \rightarrow {}^1A_{2g}$	450	22,200	350
Ni(Sal en)	$^1A_1 \rightarrow {}^1B_1$	540	18,500	130
Ni(diethyldithiocarbamate)$_2$ (*19*)		625	16,000	130

All spectra are for $CHCl_3$ solutions. DMG = dimethylglyoxime; DϕG = diphenylglyoxime; (Sal en) = (*o*-$OC_6H_4CH{=}NCH_2$-)$_2$.

These complexes have, at the most, three bands, the first of which appears in the range 15,000–18,000 cm^{-1}. The second and third are often not observed due to the high absorption of the ligands in the ultraviolet. The extinction coefficients of the bands observed are relatively high, usually in the range 90–350.

Tetrahedral Complexes

Only a few complexes are presently considered tetrahedral. One, found in the fused salt mixture of $NiCl_2$ and LiCl by Gruen and McBeth (*10*) is $NiCl_4^=$. Another, $Br_2Ni(P\phi_3)_2$ was discovered by Venanzi (*32*). Certain portions of the spectrum of $NiCl_4^=$ have been determined. As may be seen from Table 5, it is not unlike the spectra observed for diamagnetic square planar complexes.

Table 5. The Spectrum of $NiCl_4^=$

λ (mμ)	ν (cm^{-1})	E
655	15,250	~160
705	14,200	~160

However, Ballhausen (*1*) has calculated that *Dq* for tetrahedral nickel complexes should be about $^4/_9$ *Dq* for octahedral complexes. In general, *Dq* for octahedral complexes ranges from 800–1050 cm^{-1}. If this is the case, the first absorption band for tetrahedral nickel complexes should be observed at about 5000 cm^{-1}. Gruen and McBeth have found indications of an absorption in this region, but have not determined the spectrum carefully (*11*).

The Assignment of Structure on the Basis of Spectra

It is obvious from Tables 3, 4, and 5, and Ballhausen's predictions, that the spectra of octahedral, square planar, and tetrahedral nickel complexes are quite different. The difference is sufficient to distinguish between the three possible structures in most cases. For example, a considerable number of so-called "tetrahedral-cage" ligands, those whose geometry requires a tetrahedral distribution of metal bonds, are known. One of these, $N(CH_2\ CH_2\ NH_2)_3$, has been studied by Jorgensen (*16*). The spectrum observed for the nickel complex, given in Table 6, may be compared with that of the compounds in Tables 3, 4, and 5. It is obvious that the complex is octahedral.

Table 6. The Spectra of "Tetrahedral Cage" Complexes of Nickel

Compound	λ (mμ)	ν (cm^{-1})	Intensity
$Ni(tren)(H_2O)_2^{++}$	952	10,500	15.5
	781	12,800	6.3
	562	17,800	9.3
	360	27,800	12.0
$Ni(tren)(NH_3)_2^{++}$	910	11,000	12.2
	785	12,750	7.0
	550	18,200	10.1
	355	28,200	13.0
Ni(tren) (en) $^{++}$	910	11,000	11.0
	800	12,500	8.1
	535	18,700	8.8
	345	29,000	14.2

All spectra were measured in water solution. En = ethylenediamine; tren = β,β′,β″-triaminotriethylamine.

All of these data fit into the pattern described for octahedral complexes. Furthermore, when additional ligands such as ammonia or ethylenediamine are added to the solution the bands shift toward the blue, the direction expected when a ligand with a larger electrostatic field replaces the weak-field ligand, water.

This example of the determination of structure from spectra is fairly simple; however, complications may arise because of the all too commonly assumed connection between magnetic properties and structure. As we shall see later, we are not justified in thinking of para- and diamagnetic complexes in terms of their structures, octahedral and square planar.

The essential distinction between paramagnetic and diamagnetic complexes is the difference in the ground state of the metal ion. In Figure 5 the lowest energy state for an "octahedral" complex is the $^3A_{2g}$ (triplet) state whereas the lowest energy state for the "square planar" complex as shown in Figure 6 is the $^1A_{1g}$ (singlet) state. These low energy states are the ground states of the nickel ion. Of course, the $^3A_{2g}$ state is the spin-free state while the $^1A_{1g}$ state is the spin-paired state. Figure 6[8] shows that the two possible ground states for the nickel ion are not completely disconnected from each other. There is a cross-over point, indicated by the arrow, at which the two states have equal energies. On either side of this point the nickel ion would have a different ground state. For an ion very close to the cross-over point a slight change in μ or *R* would cause a change in the ground state, with a resultant change in magnetism. Figure 7 (*17*) tells us the minimum field conditions, values of μ at the cross-over point (also indicated by arrows) necessary for the preservation of the $^1A_{1g}$ (singlet) ground state for certain values of *R*. The critical values of *R* and μ are also summarized in Table 7 (*17*).

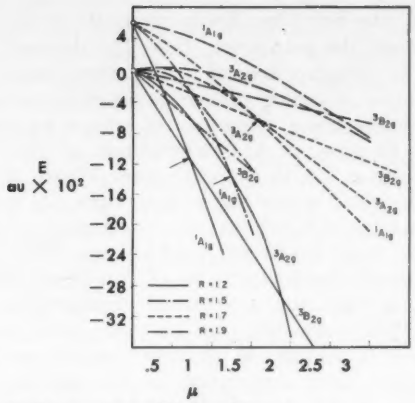


Figure 7. Singlet ground state ($^1A_{1g}$) conditions.

Table 7. Minimum Field Strength Conditions for Preservation of the $^1A_{1g}$ (singlet) Ground State in Four Coordinate D_{4h} Symmetry

R (Å)	μ (au)
1.2	0.70
1.5	1.02
1.7	1.70
1.9	>3.0

To illustrate, in Table 7 or Figure 7 we find that if *R* is 1.2 Å then μ must be 0.7 or larger for the preservation of the spin-paired singlet ground state. If μ is less than 0.7 the spin-free triplet state becomes the ground state. Now the complex will be paramagnetic just as octahedral complexes are. It must be emphasized that there has been no mention of two additional ligands to occupy the octahedral fifth and sixth coordination positions. There is no need for two additional ligands to make the complex paramagnetic; the structure will remain square planar. Of course, if two additional ligands are available they will take up positions in the coordination sphere.

[8] The $^3B_{2g}$ symbolism used in Figures 6 and 7 is equivalent to the $^3A_{2g}$ used in Figure 5. The superscripts on these symbols represent the multiplicity (spin paired for singlet and spin opposed for triplet). Since the symbols change with the symmetry (e.g., *cis* or *trans* planar) of the molecules but the superscripts do not, the term singlet will be used for the ^1A ground states and triplet for the ^3A or ^3B ground states. The symbols $^3B_{2g}$ and $^3A_{2g}$ represent the same state but are given different names for the square planar and octahedral symmetries.

The magnetic behavior of bis(*N*-methylsalicylaldimine)nickel(II) may be used to illustrate. This compound is diamagnetic in the solid state but on solution in benzene (a non-coordinating solvent) it is paramagnetic. This behavior has been explained by Maki on the basis of the cross-over point for the spin-paired singlet and spin-free triplet ground states of the nickel ion. In the solid, the field conditions are such that the complex is very close to the cross-over point. On solution in benzene the crystal field decreases somewhat and the cross-over point is approached even more closely. Maki suggests that near the cross-over point the two ground states may be in thermal equilibrium. This results in an intermediate magnetic moment for the complex. The intermediate magnetic moments exhibited by other compounds may be explained on this basis.

Of course, exactly the reverse situation is also likely to happen. If a spin-paired and square planar molecule is dissolved in a coordinating solvent it may or may not undergo a change in magnetism. The entrance of the solvent into the fifth and sixth coordination position will raise the energy of the dz_2 orbital. At the same time, the ligands around the square plane will be repelled. If they move out past the minimum *R* for preserving the singlet ground state the complex will become spin-free and octahedral, although, depending upon the entering ligands, it may be a distorted octahedron.

The result of the mechanism described above depends upon the nature of the entering ligands and on those already coordinated. If the crystal field of the entering ligands is large relative to that of the ligands in the plane of the molecule, the spin-free triplet ground state octahedral molecule will be produced. If the reverse is true, the complex will remain in a spin-paired singlet ground state but the fifth and sixth coordination positions will still be occupied. The complex is then spin-paired and the singlet ground state octahedral, but distorted in the fifth and sixth positions. If these arguments are correct, a spin-free square planar complex and a spin-paired distorted octahedral complex are possible. Structures of this type will show slightly different spectra. Some examples are listed in Table 8 (*18*).

For example, solid bis(*N*-methylsalicylaldimine)-nickel(II) is diamagnetic and shows four bands. The intensities of the first two bands are very weak and the bands are assigned by Maki as the spin forbidden transitions $^1A_g \rightarrow {}^3A_g$ and $^1A_g \rightarrow {}^3B_g$ so the ground state is ^1A_g (singlet).

The spectra of spin-paired complexes with a singlet ground state do not usually show these small bands. They are characteristic of a nickel ion in the triplet ground state. The intense bands characteristic of spin-paired singlet ground state square planar complexes are also present. It seems that a plausible interpretation would be that the complex, even in the diamagnetic solid, is very close to the cross-over point between the diamagnetic singlet and paramagnetic triplet ground states. As Maki suggests, these two ground states may even be in thermal equilibrium. The isolation of the paramagnetic form of this complex supports this explanation (*12*).

The spectrum of the chloroform solution shows that

Table 8. Spectral Changes Illustrating the Transition Between Singlet Ground State Square Planar and Triplet Ground State Octahedral

Compound	Transition	λ (mμ)	ν (cm^{-1})	Optical density or *E*
Ni (sal me im)$_2$	$^1A_{1g} \rightarrow {}^3A_g$	1180	8,500	0.025
solid	$^1A_{1g} \rightarrow {}^3A_g$	1140	8,750	0.035
diamagnetic	$^1A_{1g} \rightarrow {}^1B_{2g}$	590	16,900	0.43
	$^1A_{1g} \rightarrow {}^1B_{1g}$	499	20,000	0.56
sal me im Ni	$^3B_2g \rightarrow {}^3B_{1g}$	1150	8,700	3.3
$CHCl_3$	$^3B_{2g} \rightarrow {}^1B_{2g}$	610	16,400	100
moment—2.3 B.M.	$^3B_{1g} \rightarrow {}^1B_{1g}$	490	20,200	150
sal me im Ni	$^3B_{2g} \rightarrow {}^3B_{1g}$	960	10,400	14.1
pyridine	$^3B_{2g} \rightarrow {}^1B_{1g}$	785	12,750	4.2
moment—3.1 B.M.	$^3B_{1g} \rightarrow {}^3B_{2g}$	571	17,500	11.5
sal en Ni	$^1A_1 \rightarrow {}^1B_1$	540	18,500	130
$CHCl_3$	.....			
diamagnetic	.....			
sal en Ni	$^1A_1 \rightarrow {}^3B_1$	820	12,200	1.4
pyridine	$^1A_1 \rightarrow {}^3B_2$	675	14,800	1.4
diamagnetic	$^1A_1 \rightarrow {}^1B_1$, $^1B_2$	540	18,500	110
(3-0 me sal en)Ni		775	12,900	1.1
$CHCl_3$	.....	560	17,850	114
(3-0 me sal en)Ni	.....	825	12,100	4.1
pyridine		775	12,900	3.9
		550	18,200	128

Sal me im = *o*-$^-$OC$_6$H$_4$CH=NCH$_3$; sal en = (*o*-$^-$OC$_6$H$_4$CH=NCH$_2$-)$_2$; 3-0 me sal en = [*o*-$^-$C$_6$H$_3$(OCH$_3$)CH=NCH$_2$-]$_2$.

the crystal field has decreased slightly and the complex has crossed over into the triplet ground state. The spectrum is now still a composite of the triplet and singlet components and the complex is now paramagnetic (2.3 Bohr Magnetons). In pyridine, the complex is well into the triplet ground state region of the diagram and the spectrum becomes characteristically triplet ground state octahedral. The position and intensities of these bands correspond very well to those listed in Table 3.

The spectrum of α,α′-(ethylenedinitrilo)di-*o*-cresolato nickel(II) in $CHCl_3$, where the complex is diamagnetic, is characteristic of a singlet ground state square planar complex as far as band position and intensity go. But, in pyridine where the complex is still diamagnetic, the very weak bands which were observed in the spectrum of solid diamagnetic bis(*N*-methylsalicylaldiminato)nickel(II) begin to appear. The intense band characteristic of singlet, square planar complexes is still present. This complex is approaching the cross-over point. Solution in a more basic solvent should show a characteristic triplet ground state octahedral spectrum.

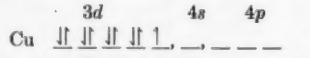
The spectra of α,α′-(ethylenedinitrilo)bis (3-methoxy-*o*-cresolato)nickel(II) in $CHCl_3$ and pyridine show the compound to have the same structure as α,α′-(ethylenedinitrilo)di-*o*-cresolato nickel(II) described above. Hence, the methoxy compound also should show the characteristic triplet ground state octahedral spectrum in a more basic solvent. The pattern here is very similar and illustrates the transition between singlet ground state square planar (diamagnetic) and triplet ground state octahedral (paramagnetic) very clearly.

In summary, the spectrum of a complex which is triplet ground state octahedral is clearly distinct from the spectrum of a complex which is singlet ground state square planar. It is also possible to have a complex which is triplet ground state square planar as well as one which is singlet ground state octahedral. The

spectra of complexes which are near the cross-over point are composites of both singlet and triplet ground states. Errors in the assignment of structure from spectra for this type of complex may be eliminated by examination of the complete spectra.

The Spectra of Copper Complexes

The electronic structure of Cu(II) may be represented



for which the valence bond theory predicts that the odd electron of the $3d$ level will be promoted to a higher energy orbital in order that dsp^2 hybridization may take place. However, as a consequence of such a promotion Cu(III) should be easily prepared. It is not. An alternative is to use a $4d$ orbital in the hybridization but it is difficult to predict whether this orbital is of suitable energy to be used in the hybridization. Neither of these explanations is necessary if the crystal field theory is applied.

Orgel (*23*) first pointed out the application of crystal field theory to copper complexes. According to the theory the complexes of copper are basically square planar with the odd electron occupying the $d_{x^2-y^2}$ orbital. If any additional ligands are available they would take up the fifth and sixth coordination positions. However, because the d_{z^2} always contains a pair of electrons, in most copper complexes the fifth and sixth ligands will not be able to approach the copper as closely as the ligands in the plane, and thus the complex will have a tetragonal structure.

The spectra of copper complexes are interesting in that they permit a correlation of the observed spectra with the orbitals involved in the transition. This may be done by comparing the spectrum of a copper complex in a variety of solvents. Belford (*4*) has measured the spectrum of copper acetylacetonate in several solvents. Before presenting the results we may follow the reasoning used to predict the results.

The square planar energy level diagram for one or nine d electrons is similar to that given in Figure 8. As ligands five and six (solvent molecules) approach the copper the d_{z^2}, d_{xz}, and d_{yz} orbitals will increase in energy. At the same time the ligands in the original plane will be caused to move away from the copper thereby decreasing the energy of the $d_{x^2-y^2}$ and d_{xy} orbitals by about the same amount. The effect of this on the three possible transitions then will be:

$d_{z^2} \rightarrow d_{x^2-y^2}$	shift toward the red
d_{xz}, $d_{yz} \rightarrow d_{x^2-y^2}$	" " " "
$d_{xy} \rightarrow d_{x^2-y^2}$	no appreciable effect

These shifts are illustrated in Figure 8 as the transition

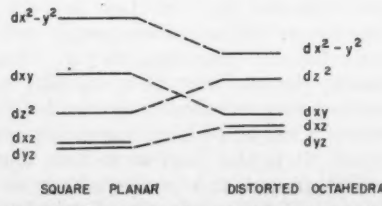


Figure 8. Transition from square planar to distorted octahedral.

from the square planar to the octahedral energy level diagram. Examination of the experimentally observed spectra in Table 9 shows that these effects are observed when one proceeds from a weakly coordinating solvent to a strongly coordinating solvent.

Table 9. The Effect of Solvent on the Spectrum of Cu(acetylacetonate)$_2$

Solvent	ν_1 (cm^{-1})	ν_2 (cm^{-1})	ν_3 (cm^{-1})
$CHCl_3$	18,810	15,190	...
1,4-Dioxane	17,500	15,100	13,500
n-Pentanol	17,100	15,200	13,000
Pyridine	15,900	14,800	12,100
Piperidine	15,100	14,800	11,300

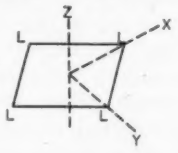
$\nu_1 = d_{xz}$, $d_{yz} \rightarrow d_{x^2-y^2}$; $\nu_2 = d_{xy} \rightarrow d_{x^2-y^2}$; $\nu_3 = d_{z^2} \rightarrow d_{x^2-y^2}$.

Thus two important conclusions result from the examination of the spectra of copper complexes in different solvents. One is that copper complexes can coordinate more than four ligands; the other identifies the absorption bands in terms of orbital transitions.

The last point is important in that it enables one to have a physical picture of the transitions taking place between two separate orbitals. The symbolism used in the assignment of the bands for nickel complexes in Tables 3 and 4 does not seem to allow such a picture. In the next section the meaning of these symbols will be discussed and an interpretation of the transitions in terms of a set of orbitals will be introduced. Since the relationship between the symmetry symbols and atomic orbitals is simplest for copper complexes these will be used first. Then the symbolism appropriate for nickel complexes will be developed.

The Meaning of the Symmetry Symbols

The symmetry symbols are dependent upon the symmetry of the molecule under consideration. As a specific example a square planar molecule will be used to illustrate where L is the ligand.



The symmetry which a molecule possesses is summed up very conveniently in what is called the point-group representation. The first step in determining the symmetry symbols appropriate for a complex then is to determine the point group of the molecule. This will be done for a square planar molecule. The procedure for determining the point group representation for other structures will not be discussed but may be found in any book on crystallography (*34*).

In a square planar molecule where the coordinating atoms are all the same the relative positions of these atoms will be the same after a rotation of 90° about the z axis; this is then termed a fourfold rotation axis. If the molecule has $2n$ twofold rotation axes (rotation of 180°) perpendicular to the major axis then the point group symbol D_4, is assigned to it. If the molecule also has a plane of symmetry, σ perpendicular to the fourfold axis the symbol becomes D_{4h}. A square planar molecule has several other elements of symmetry which will be important later. These are shown in Figure 9 along with those discussed above.

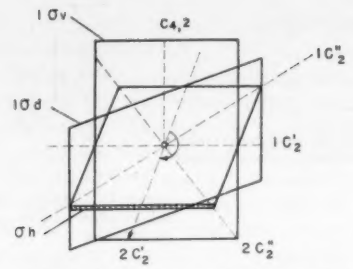


Figure 9. The symmetry elements of a square planar molecule.

In Table 10 the meaning of these elements of symmetry is given.

Table 10. The Symmetry Operations

Symbol	Meaning
i	Inversion through a center of symmetry
C_4	Fourfold axis of rotation
C_2'/C_2''	Twofold axis of rotation
σ	Plane of symmetry, σ_h if the plane is perpendicular to the principal axis, σ_v if the plane contains the principal axis, and σ_d if the plane bisects the angle made by two twofold rotation axes
E	Identity
S_4	C_4 followed by inversion through i

Once the point group for the molecule has been established the character table for the particular point group may be found in appropriate references (*8*, *14*). The character table for the D_{4h} symmetry is given in Table 11.

Table 11. Character Table for D_{4h}

Symmetry representations	Elements of symmetry: E	C_2	$2C_4$	$2C_2'$	$2C_2''$	i	σ_h	$2S_4$	$2\sigma_v$	$2\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2g}	1	1	1	−1	−1	1	1	1	1	−1
A_{2u}	1	1	1	−1	−1	−1	−1	−1	1	1
B_{1g}	1	1	−1	1	−1	1	1	−1	1	−1
B_{1u}	1	1	−1	1	−1	−1	−1	1	−1	1
B_{2g}	1	1	−1	−1	1	1	1	−1	−1	1
E_{1g}	2	−2	0	0	0	2	−2	0	0	0
E_{1u}	2	−2	0	0	0	−2	2	0	0	0

The derivation of tables such as this depends upon group theory, a subject very much beyond the scope of this discussion. It need not be given however, since the use of the table, as we shall use it, does not depend upon the derivation. Before illustrating the use of the table its various parts must be described.

The symmetry symbols at the top have the same meaning as in Table 10. The letters at the left (those used in the energy level diagrams) represent the symmetry of the orbital under consideration. The numbers in the body will be mentioned shortly. The table may now be used to determine the symmetry symbols which represent the d orbitals. To do this we must perform the symmetry operations listed in the table on each d orbital. When this is done the orbital either reproduces itself (the orbital is the same after the operation as it was before) or it does not reproduce itself. In the body of the table 1 indicates reproduction and −1 indicates non-reproduction.

To illustrate consider the d_{z^2} orbital from Figure 1. The operation of all the symmetry operations reproduces the orbital so the symbol representing the symmetry of the d_{z^2} orbital is A_{1g}. But, the $d_{x^2-y^2}$ orbital

on rotation through C_4 does not reproduce itself so the symmetry representation cannot be A_{1g}.

On performing the remaining operations on the $d_{x^2-y^2}$ orbital we find that the symmetry representation is B_{2g}. In a similar fashion, the symmetry of the d_{xy} orbital is found to be represented by B_{1g}. The d_{xz} and d_{yz} orbitals are doubly degenerate and the symmetry symbol would be E_{1g}. These will not be important to further development in this point group.

The only restriction to this point in the development of the symmetry symbols has been that the molecule must be square planar. No specific central metal has been used. When a specific metal is to be used some complications arise because the orbitals used from Figure 1 are those obtained with the assumption that the angular distribution of one electron will not be affected by the presence of another electron in the d level. This will not be the case. Thus, in order to work with a system which contains more than one electron we must find a way of representing the angular distribution of an electron which is under the influence of the other d electrons present. A satisfactory (*6*), although not the best, representation may be obtained by simply multiplying the angular distribution for one electron by that for the other electrons present. For example, in a two electron system we would obtain the angular distribution of a double product wave function by multiplying the angular distribution of one electron by that of the other. In a system such as copper(II) with nine electrons, it would be necessary to multiply the angular distribution of each electron by that representing the eight other electrons present. This would be almost impossible; as it turns out, it is not necessary.

Since the total number of possible d electrons is 10, we may think of the d level of a copper ion as containing one hole instead of nine electrons. In considering the effect of an electrostatic field of ligands on the d orbitals we would now determine the effect on one hole, not the effect on nine electrons. The hole will not be repelled by the ligands but will be attracted to them. Therefore, in the ground state of the copper ion, the hole will occupy the orbital which is directed at the ligands, (e.g., the $d_{x^2-y^2}$ in the square planar structure). In an excited state, one of higher energy than the ground state, the hole will be in one of the orbitals not pointing at the ligands (e.g., the d_{xy}, d_{xz}, or d_{z^2} orbital). A transition then involves moving the hole from the ground state to the excited state.

Using this model the energy level diagram (Fig. 10) for a square planar complex may be derived as follows: When the hole is in the $d_{x^2-y^2}$ orbital it will have the

lowest possible energy. In the d_{xy} it will have a somewhat higher energy. This situation is unstable because the hole is being attracted to the ligands near the $d_{x^2-y^2}$. In the d_{z^2} it will be next highest in energy and in the d_{xz} or d_{yz} it will be highest of all. The diagram given in Figure 10 is exactly the opposite from that which would be derived for an electron. This is the way that energy level diagrams for atoms with more than five d electrons are usually represented. Figures 5, 6, and 7 are of the hole type.

From this discussion we see that a d^9 system can be handled as a d^1 system or in general a d^n system is equivalent to a d^{10-n} system. Thus, the symbols which were developed earlier for a one electron system are appropriate for copper. The orbital assignments made by Belford may now be made in terms of symmetry symbols. This is done in Table 12.

Table 12. Transitions for Cu(acetylacetonate)$_2$

$d_{xy} \rightarrow d_{x^2-y^2}$	$B_{1g} \rightarrow B_{2g}$
$d_{z^2} \rightarrow d_{x^2-y^2}$	$A_{1g} \rightarrow B_{2g}$
$d_{xz}, d_{yz} \rightarrow d_{x^2-y^2}$	$E_g \rightarrow B_{2g}$

In order to obtain the symmetry symbols appropriate for square planar nickel complexes, a two-hole system, we must obtain double wave functions and put them through the symmetry operations of the point group just as we did for the single wave functions above. Or more simply, we may multiply the single electron symmetry symbols together (multiply the number in the body of the table) to obtain the double electron symmetry symbols. This has been done in Table 13.

Table 13

$d_{z^2} \cdot d_{z^2}$	$= A_{1g} \cdot A_{1g} = A_{1g}$
$d_{x^2-y^2} \cdot d_{x^2-y^2}$	$= B_{2g} \cdot B_{2g} = A_{1g}$
$d_{x^2-y^2} \cdot d_{xy}$	$= B_{2g} \cdot B_{1g} = A_{2g}$
$d_{z^2} \cdot d_{x^2-y^2}$	$= A_{1g} \cdot B_{2g} = B_{2g}$

It is now possible to see the origin of the symmetry symbols used in Figure 6. However, in order to complete the picture it would be convenient to have plots similar to Figure 1. These may be obtained in the following manner. The angular parts of the wave function for a single electron used to obtain the plots in Figure 1 are given in Table 14 (*28*). If these are

Table 14. Single Electron Wave Functions (Angular Distribution Only, Numerical Constants Have Been Omitted)

d_{z^2}	$3(\cos^2\theta - 1)$
$d_{x^2-y^2}$	$\sin^2\theta \cos^2\phi$
d_{xy}	$\sin^2\theta \sin^2\phi$

multiplied in the manner indicated above for the symmetry symbols the expressions for the angular distribution of the two-electron wave functions are obtained. The results of such a treatment are listed in Table 15.

We now have mathematical expressions which describe the symmetry symbols representing them. The

Table 15. Double Electron Wave Functions (Angular Distribution Only)

$d_{x^2-y^2} \cdot d_{x^2-y^2}$	$\sin^4\theta \cos^2 2\phi$
$d_{x^2-y^2} \cdot d_{xy}$	$^1/_2 \sin^4\theta \sin 4\phi$
$d_{z^2} \cdot d_{x^2-y^2}$	$3 \cos^2\theta \sin^2\theta \cos 2\phi - \sin^2\theta \cos 2\phi$

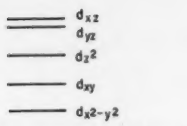


Figure 10. Energy level diagram for a one hole system, square planar symmetry.

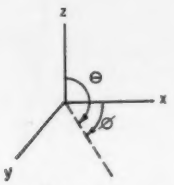


Figure 11. Relation between polar coordination angles and cartesian coordinates.

angles in these expressions are polar coordinate angles and their relationship to cartesian coordinates is shown in Figure 11. With the help of polar coordinates, these expressions can be plotted for various values of the angles. The shapes obtained in this way are shown in Figure 12. Thus, we have a new set of orbitals which describe the symmetry of the two electron wave functions. The difference between these new orbitals and those shown in Figure 1 is only slight.

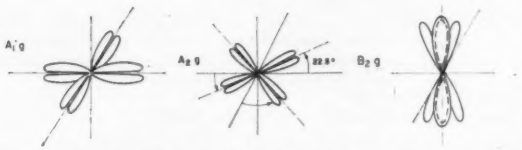


Figure 12. Angular distribution of double product wave functions. A_{1g} is similar to two $d_{x^2-y^2}$ orbitals one set on top of the other. A_{2g} is similar to two d_{xy} orbitals one set on top of the other. B_{2g} has two sets of lobes, one in the x_2 plane and one in the yz plane. The dotted lobes represent the ones which tip downward behind the paper. Each of the lobes is double. However, this situation and the details around the origin have been omitted for simplicity.

The assignments given in Table 4 for square planar nickel complexes such as bis(dimethylglyoximato)-nickel(II) may now be pictured as transitions between sets of orbitals. The transition $A_{1g} \rightarrow A_{2g}$ essentially represents the movement of a hole from the $d_{x^2-y^2}$ to the d_{xy} orbital while the $A_{1g} \rightarrow B_{2g}$ represents the transition from essentially the $d_{x^2-y^2}$ to the d_{z^2} orbital. Electron transitions will of course be reversed.

Summary

The spectrum of a complex is characteristic of the ground state of the metal ion. Characteristic features of the nickel(II) spectra are;

Triplet ground state nickel(II)
- Sometimes three but more often four absorption bands
- Low intensity E = 1–50
- ν_3/ν_1 = 1.6–1.8
- Absorption maxima fall in the ranges 8,000–11,000; 12,000–13,000; 15,000–19,000; 25,000–29,000 cm^{-1}

Singlet ground state nickel(II)
- As many as three but sometimes only two or one bands depending upon ultraviolet absorption
- High intensity 90–350
- Absorption maxima fall in the range 14,000–18,000 and to higher frequencies

The spectra of tetrahedral nickel complexes are not well known but the first absorption band will be observed at about 5000 cm^{-1}. The extinction coefficients of the observed bands are larger than those observed for the triplet ground state.[9] Using these generalities and

[9] COTTON, F. A., AND GOODGAME, D. M. I., have recently assigned a tetrahedral structure to the ion $[(C_6H_5)_3PNiBr_3]^-$ on the basis of its spectrum, *J. Am. Chem. Soc.*, **82**, 2967 (1960).

reasonable care the structure of a complex may be determined from its spectrum.

The spectra of copper complexes indicate the existence of six coordinate copper and allow an assignment of the absorption bands in terms of atomic orbitals. Atomic orbitals may also be related to transition assignments for d^2 or d^8 systems by the method described. This may be extended to any other d^n system.

The application of the crystal field theory to nickel and copper complexes described here represents only a small fraction of the outstanding work accomplished with the theory. Other aspects, not mentioned here, have been the subject of a considerable amount of research. For example, the theory provides a method of distinguishing between *cis* and *trans* isomers. It has also been used with a great deal of success in the reaction mechanism field. Then of course the original application of the theory to magnetic properties illustrates still another application. The variety of applications adequately illustrates the importance of this theory (*3, 9, 25*).

The authors feel that a knowledge of the crystal field theory is an essential part of the training of inorganic and physical chemists. It is hoped that this paper will contribute to the accomplishment of this task.

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John R. Ferraro
Argonne National Laboratory
Argonne, Illinois

Inorganic Infrared Spectroscopy

The infrared spectroscopic study of organic compounds has been known for a number of years. However, the application to inorganic compounds had a rather late start. Most of the early work on the spectra of inorganic compounds concerned itself with the Raman method. Some reflection infrared methods (*1*) were used as early as 1930. The lack of high resolution spectrophotometers, plus the fact that adequate specimen preparation was difficult, delayed progress in this field. Since large particle size gave considerable scattering losses most early infrared spectra of inorganic compounds gave broad, indeterminate absorptions, as compared to the sharp spectra obtained with organic compounds.

With the introduction of commercial high resolution spectrophotometers and new methods of specimen preparation, such as Nujol mulls, pressed discs (*2–4*), and recently the rare gas matrix isolation method (*5*), the spectra obtained were found to be excellent. Revival of interest in inorganic compounds took place. Lecompte must be given credit for a considerable amount of this revival. He and his co-workers examined numerous inorganic compounds; the studies appeared

Based on work performed under the auspices of the U. S. Atomic Energy Commission. Paper presented at the Infrared Spectroscopy Institute, Canisius College, Buffalo, N. Y., August, 1960.

in a series of papers in 1951 (*6*, *7*). A very important paper appeared in 1952 by Miller and Wilkins (*8*), which added further impetus to this revival. They examined the spectra of over 150 salts in the sodium chloride region, and their correlation for analytical and identification work proved excellent. The last eight years have seen a tremendous development in the progress in inorganic infrared spectroscopy.

It is the purpose of this paper to point out some of this development with a particular emphasis on the application of infrared spectroscopy in solving various problems in inorganic chemistry. The paper is in no way intended to be a complete bibliographical report on this subject; it attempts to serve only as an introduction.

Qualitative and Quantitative Analysis

It is beyond the scope of this paper to present elaborate details concerning the qualitative and quantitative analysis of inorganic compounds utilizing infrared methods. When used with other physical measurements, the infrared method aids inorganic analysis. The numerous reviews (*9*, *10*) in the literature of quantitative organic analysis cover principles also appropriate for analysis of inorganic compounds.

Miller and Wilkins (*8*) reported the spectra of numerous inorganic compounds. It is apparent from their work that a number of discrete regions of absorptions, characteristic of the type of anion present, existed. From their correlations, qualitative identification of various inorganic anions can be made. Similar correlations have since been made for various other inorganic compounds, and these can aid in making qualitative identifications. Several examples of quantitative infrared analyses have been reported. Hunt, *et al.* (*11*, *12*) analyzed a number of rocks and minerals. Corbridge (*13*) has done some quantitative work on condensed phosphates.

Structure of Complex Inorganic Molecules

Infrared spectroscopy has assisted in the determination of the structure of certain complex inorganic molecules, such as the metal carbonyls, inter-halogen compounds, boron hydrides, and nitrogen oxides. The practice used has been to compare the observed spectrum with the spectrum expected for an assumed model, on the basis of group-theory-derived selection rules. The dependability of this procedure depends on the degree of reliability of the observed spectrum. It is not at all satisfactory to use this method if the observed spectrum is poorly resolved. In addition, failure to observe as many bands as are required by the selection rules is no basis to reject a certain model. The metallic carbonyls illustrate this point well.

Metallic Carbonyls. Sheline (*14–16*) has examined the infrared spectra of the iron carbonyls, $Fe_2(CO)_9$, $Fe_3(CO)_{12}$, and $Fe(CO)_5$. The carbonyls of cobalt (*17*, *18*), $Co_2(CO)_8$, and $Co_4(CO)_{12}$, have also been studied. X-ray diffraction data (*19*) has indicated that in some of these carbonyls there are two kinds of carbonyl groups; the "bridging" type and the "end" type. Infrared data of some of these compounds has shown absorptions in the 2000 cm^{-1} region, and this has been attributed to the "end" carbonyls; while another absorption was found in the 1800 $cm.^{-1}$ region, and this was attributed to the "bridged" carbonyl group.

The assignment of the band in the region of 1800 cm^{-1} as a bridged carbonyl group finds confirmation from chemical means (*20*). Two bridging groups can be replaced by one molecule of acetylene, and the 1800 cm^{-1} band disappears.

Iron enneacarbonyl, $Fe_2(CO)_9$ was found to have C—O stretching frequencies at 2080 and 2034 cm^{-1} due to the terminal carbonyl groups, and an absorption at 1828 cm^{-1} due to the bridged group (*16*). The structure proposed for this compound was that shown in Figure 1.

Diffraction data for iron tetracarbonyl $Fe_3(CO)_{12}$ are not available. From infrared studies (*15*) the structure proposed is shown in Figure 2, since bands are found at 2020, 2043, and 1833 cm^{-1}. Cotton (*15*) has found an additional band at 1997 cm^{-1} using LiF optics, which indicate that Sheline's structure is incorrect. The proof of this structure is thus still open to discussion.

The recent work of Cotton and Monchamp (*21*) in regard to the carbonyls of cobalt [$Co_2(CO)_8$ and $Co_4(CO)_{12}$] is of particular importance. Original work with $Co_2(CO)_8$ had shown bands at 2034, 2054, 2077, and 1858 cm^{-1}; from this it was inferred that both "end" and "bridging" carbonyls existed in the molecule, and that the structure proposed (Fig. 3) was that of two trigonal bipyramids joined at an edge (*17*, *18*). Using calcium fluoride optics, Cotton, *et al.* (*21*), found bands at 2075, 2064, 2047, 2035, 2028, 1867, and 1859 cm^{-1}.

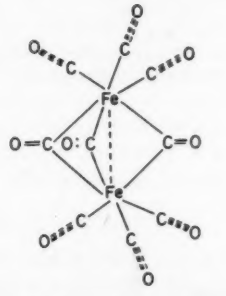


Figure 1. Proposed structure for $Fe_2(CO)_9$.

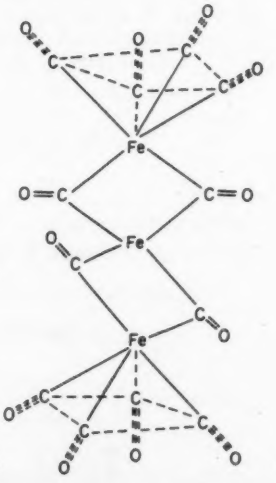


Figure 2. Proposed structure for $Fe_3(CO)_{12}$.

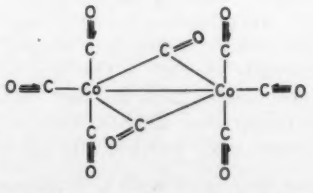


Figure 3. Proposed structure for $Co_2(CO)_8$, D_{2h} symmetry, trigonal bipyramid (*17*).

The appearance of five terminal fundamental frequencies and two bridging bands ruled out all of the previously proposed structures. In a similar fashion the structure proposed for $Co_4(CO)_{12}$ was found to be in error (*21*). The new structure proposed has been substantiated by X-ray studies (Fig. 4) (*22*).

The manganese and rhenium compounds $[M_2(CO)_{10}]$ do not possess bands in the 1800–1900 cm^{-1} region and are believed, as a result, not to contain a bridged structure (*23*). X-ray diffraction data has recently confirmed this (*24*).

The interpretation of the structures of the simpler carbonyls was also aided by infrared spectroscopy. Chromium, molybdenum, and tungsten form hexacarbonyls of the type $M(CO)_6$. Electron diffraction and X-ray studies have indicated a regular octahedral structure (*25*, *26*). Infrared measurements have confirmed this.

The infrared spectrum of $Fe(CO)_5$ has shown that the compound has a trigonal bipyramid structure (*16*). The assignment of the observed frequencies of the gas was successfully made on the basis of a trigonal bipyramid model (Fig. 5). Recently (*27*), the stereochemistry of five coordinate compounds of the type $LFe(CO)_4$, $L_2Fe(CO)_3$ where L is Ph_3P, Me·NC, Et·NC, Ph·NC, Bu·NC, and $(PhNC)_5Co^{+1}$ has been examined. By means of the infrared spectra and comparison with the selection rules, the configurations were concluded to be very probably as in $Fe(CO)_5$, trigonal bipyramid.

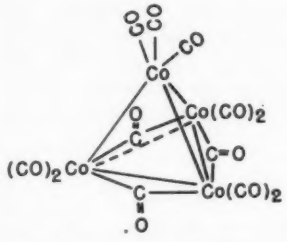


Figure 4. Structure of $Co_4(CO)_{12}$ according to Corradini and Ercoli (22).

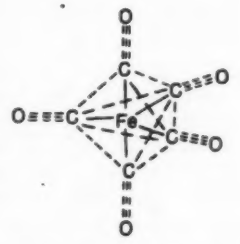
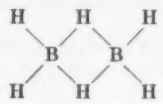


Figure 5. Proposed structure for $Fe(CO)_5$.

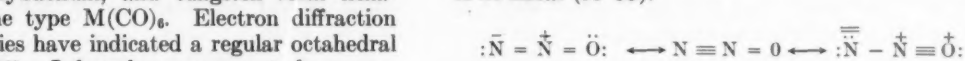
Interhalogen Compounds. Several of these compounds have been investigated by the infrared method and structures elucidated. The compound IF_5 illustrates how Raman and infrared spectra can together aid in structure determination. The Raman spectrum of the liquid (*28*) and the infrared spectrum of the gas (*28*) were measured. Lord, *et al.*, compared their observations with the predicted number of frequencies for seven possible symmetries for the molecule (Table 1).

Structures 5, 6, and 7 are immediately eliminated, as are structures 1 and 2. Thus, the structure of IF_5 is either 3 or 4, (4 being a tetragonal pyramid) providing the spectrum is highly resolved. In a similar way the structure of IF_7 was postulated to be a pentagonal bipyramid.

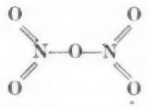
Boron Hydrides. Infrared examination of diborane (B_2H_6) showed that it had eight bands which appear to be fundamentals (*29*). If the structure is of a bridge type, then the selection rules predict eight infrared vibrations. Aluminum borohydride, $Al(BH_4)_3$ was also investigated by infrared and results (*30*) were interpreted on the basis that the structure has hydrogen bridges as in diborane.



Oxides of Nitrogen. The establishment of structures for the various oxides of nitrogen has also been helped by infrared measurements. Nitrous oxide was shown to be linear (*31–33*).



Nitrogen tetroxide has been studied in the solid, liquid, and the vapor state and has led Sutherland (*34*) to predict a planar structure. Recent confirmation of this was made by Snyder and Hisatsine (*35*). Nitrogen pentoxide was shown to have the structure in the liquid state (*36*).



Coordination Compounds

Infrared spectroscopy has been a very useful tool in the field of coordination chemistry. It has aided in the problems of structure determination, *cis-trans* isomerism, metal-ligand site attachment, and in determining bond types in these complex molecules. Only several examples in which the infrared spectra of coordination compounds have been instrumental in solving the aforementioned problems will be presented. Numerous others are known, and may be found in the literature.

Certainly a large effort in this field has been made by the group at Notre Dame, including Quagliano and Mizushima.

The structural isomerism arising in the complex ions, nitropentamminecobalt(III) $[Co(NH_3)_5NO_2]^{++}$, and nitritopentamminecobalt(III) $[Co(NH_3)_5ONO]^{++}$ has been reported (*37*). From analogy with the colors of compounds known to possess M—O or M—N links, the stable yellow-brown form was considered to have the Co—N link, while the unstable red form was considered to have a Co—O link. The verification of these postulates has now been accomplished by infrared techniques (*38*). The infrared assignments

Table 1. Application of the Vibrational Selection Rules to the Possible Structure of IF_5 (28)

Structure	Point group	Total frequencies	Raman spectrum		Infrared spectrum	Coincidences	
			Total	Polarized		Total	Polarized
1	D_{3h}	7	3	1	3	0	0
2	D_{3h}	8	6	2	5	3	0
3	C_{5v}	7	7	2	4	4	2
4	C_{4v}	9	9	3	6	6	3
5	C_{3v}	8	8	4	8	8	4
6	C_{2v}	12	12	5	11	11	5
7	C_s	12	12	8	12	12	8
Observed		9	8	3	4	3	2

made for these isomers are shown in Table 2.

Table 2. Differences in Infrared Absorption of the Ions $[Co(NH_3)_5NO_2]^{+2}$ and $[Co(NH_3)_5ONO]^{+2}$

	Cm^{-1}	Assignment
$[Co(NH_3)_5NO_2]^{+2}$	1430	NO_2 (st.) antisym.
	1315	NO_2 (st.) sym., and NH_3 def. sym.
	825	NO_2 (def.)
$[Co(NH_3)_5ONO]^{+2}$	1460	O—N—O (st.) antisym.
	1065	O—N—O (st.) sym.

This was done by observing the growth of peaks at 1430 cm^{-1}, 1315 cm^{-1}, and 825 cm^{-1}, with a decrease initially in intensities of the absorptions at 1460 cm^{-1} and 1065 cm^{-1} as freshly prepared red $[Co(NH_3)_5ONO]Cl_2$ aged. Eventually the peaks at 1460 cm^{-1} and 1065 cm^{-1} disappeared, and the spectrum became that of the yellow brown $[Co(NH_3)_5NO_2]Cl_2$.

Infrared spectroscopy has proved helpful in determining the site of attachment of the metal to the ligand (*39*). In the coordination compounds involving urea and thiourea as ligands, the problem involved is whether one has a metal-nitrogen bond or a metal-oxygen bond, in the case of urea. The infrared spectra of these complexes showed that urea formed metal-nitrogen bonds with Pt(II) and Pd(II), and metal-oxygen bonds with Cr(III), Fe(III), Zn(II), and Cu(II). These conclusions were reached by a comparison of the spectra of the complexes with that of free urea. If the coordination involves M—O bonds the spectrum would be expected to differ only slightly from that of urea. The C=O absorption would shift toward lower frequency [the C=O absorption region at 1700 cm^{-1} is blank in the Cr(III), Fe(III), Zn(II), and Cu(II) compounds, while in free urea it is at 1683 cm^{-1})]. If metal-nitrogen bonds are involved, then the spectrum is significantly different from that of the free urea molecule. The NH stretching, NH deformation, and CN vibrations would be expected to shift toward lower frequencies, as indeed they do in the Pt(II) and Pd(II) compounds. In addition, the absorption due to the carbonyl group is shifted to 1720 cm^{-1}, because of the blocking of resonance between the bonded nitrogen and the C=O group, as one would expect.

Similar comparisons of the spectra of the metal-thiourea complexes with that of free thiourea showed that all metal bonds were to sulfur (*40*). The spectra were all similar to the spectrum of thiourea, with the exception that the C=S frequency was shifted to lower values.

Infrared spectroscopy has aided in distinguishing between *cis* and *trans* isomerism in inorganic coordinated compounds. For example, *cis*- and *trans*-dinitrotetraammine cobalt(III) chloride, $[Co(NH_3)_4(NO_2)_2]Cl$, can readily be distinguished by their spectra (*41*). Fewer absorption peaks were present in the *trans* compound than in the *cis*. This can be a direct consequence of the selection rules, since the *trans* complex has a center of symmetry while the *cis* complex does not; therefore the *trans* compound might be expected to give a less rich spectrum. However, only one example was given. It would be of interest if other *cis-trans* isomers gave the same results.[1]

Organometallic Compounds

Salts of Carboxylic Acids. The salts of the carboxylic acids have been extensively studied by Lecompte (*42–45*). When dealing with salts of acids, the characteristic carbonyl absorption is lost and is replaced by two bands between 1550–1610 $cm.^{-1}$ and between 1300–1400 cm^{-1} corresponding to the antisymmetrical and symmetrical vibrations of the COO^- group.

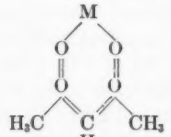
In the solid state, the two frequencies vary with the nature of the metallic ion. For mono- and divalent elements there is a linear relationship between the electronegativity of the element and the asymmetric stretching frequency (*46*). Stimson (*47*) has also noted similar dependencies in salts of substituted benzoic acids.

Salts of Phosphorus Oxy-Acids. The spectra of a number of inorganic salts of the phosphorus oxy-acids were measured in the NaCl region (*13, 48*). The absorptions of each type of anion were characteristic, and correlations (*48*) were suggested for various structural groupings in these substances. The hydrated salts all absorb in the OH region of water at 3300 and 1640 cm^{-1}. In addition, the spectra are rich in the regions of 900–1400 cm^{-1}, and these are attributed to P—O associated vibrations (e.g., P=O stretching, ionic POO^-, PO_3^{-2}, and P—O—P).

Metal Complexes of Acetylacetone. A number of metal complexes of acetylacetone have been prepared and studied by infrared methods (*49–56*). The infrared results with acetylacetone are consistent with a conjugated chelate structure resonating between forms I and II on

I II

It would be expected that coordination to a metal (III) would shift the carbonyl frequency to lower values; shift the C—H stretching absorption to higher frequency (new environment more like benzene ring); the antisymmetric and symmetric methyl stretching vibrations should remain about where they are in acetylacetone; the OH . . . . O absorption should disappear. All of these expectations have been realized in the infrared spectra of these compounds. Efforts to correlate the shift of the carbonyl frequency with the strength of the complex also have been made (*55, 56*).



III

[1] An excellent review on the "Infrared Spectra of Transitional Metal Complexes" by F. A. Cotton has recently appeared in the book "Modern Coordination Chemistry" by J. Lewis and R. G. Wilkins, Interscience Publishers Inc., New York, 1960.

Phosphorus Compounds

The industrial uses of phosphorus compounds in recent years have grown rapidly. Phosphorus compounds are used in the oil industry as additives, in detergents and insecticides, in food manufacture, in water treatment, and as solvent extractants in ore processing. It is in the field of solvent extraction that many of the organophosphorus compounds have made valuable contributions recently.

The infrared study of these compounds was started by Daasch and Smith (*57*). They published spectra of 60 organophosphorus derivatives and proposed spectra-structure correlations. Bellamy and Beecher (*58*) extended these studies, as did others (*48, 59–66*). Most of this work was made on the neutral type of esters. The acidic type of esters has gained more attention in the past five years, with the groups at Argonne, Oak Ridge, and Harwell laboratories evaluating these acids as solvent extractants for various cations. In the course of this work many new acidic type organophosphorus compounds have been synthesized and subjected to infrared studies (*67*).

The infrared studies of the acidic type of organophosphorus esters of the type $(GO)_2POOH$, G'OGPOOH (where G can be alkyl, aryl, or variant thereof) have been reported (*67*). These acids have been found to be dimeric in most solvents, and intermolecular hydrogen bonding has been postulated. Despite the fact that these compounds are quite complex, the infrared spectra can be qualitatively analyzed in terms of vibrations involving the phosphorus atom and those involving the G group. The spectra are characterized by broad regions of absorption at about 2500–2700 cm^{-1} and about 2300–2350 cm^{-1} (*67, 68*); and these have been attributed to the bonded P—OH stretching motion (*57, 58*). In addition, a third, broad region appears at about 1680 cm^{-1}, which is attributed to the bonded P—OH deformation motion (*69, 70*). These regions all disappear on salt or metal complex formation, and are appropriately shifted to lower frequencies on deuteration. The P → O stretching vibration is very strong and is observed in the 1200 cm^{-1} region. The identification of this absorption is aided by salt or complex formation. The strongest absorption appears at the 1000 cm^{-1} region and is probably due to several vibrations P—O—(G) and (P)—O—G. Where G is aryl, the P—O—(G) vibration (asymmetric) appears at about 966–1010 cm^{-1} (*64*). Where G is alkyl, it is found at about 1000–1050 cm^{-1}. In aryl phosphorus acids the vibration at 1180 cm^{-1} is attributed to the (P)—O—aryl stretching motion. The various CH vibrations are located in the expected positions of the spectra (CH stretching, 2800–3100 cm^{-1}; CH deformation, 1380–1480 cm^{-1}; C=C skeletals in the aryl ring 1590–1610 cm^{-1}, and 1500–1518 cm^{-1}; CH out-of-plane vibrations in aryl phosphorus acids, 700–835 cm^{-1}).

Differentiating Between Ionic and Covalent Bonds

The use of infrared spectroscopy in differentiating between an ionic bond and a covalent bond in a complex (in the ligand-metal bond), where the ligand is nitrate, carbonate, thiocyanate, and cyanide has been reported. The method has been particularly useful in the case of nitrates and carbonates, while not so successful in the case of thiocyanates and cyanides.

Nitrates. The nitrate ion is considered to have the configuration of an equilateral triangle possessing the point group D_{3h} symmetry. In nitrate compounds in which the nitrate is covalently bound the symmetry lowers, and is changed to that of a point group C_{2v} symmetry (*71*). Thus in going from a D_{3h} symmetry to one of C_{2v} the ν_3 frequency in the symmetrical NO_3^- ion (point group D_{3h}) undergoes splitting into two new frequencies. One component is observed to shift toward higher frequency (ν_4) at about 1500 cm^{-1}, and the other toward lower frequency (ν_1) at about 1275 cm^{-1}, both of point group C_{2v} symmetry. In addition, ν_2 at about 1000 cm^{-1} appears, as does the ν_6 frequency at about 800 cm^{-1}.

Gatehouse (*72, 73*) and Quagliano (*74, 75*) have recently examined the infrared spectra of several nitratocomplexes of the transition elements, and observed the changes in symmetry occurring when the nitrate is in and out of the coordination sphere of the cation. They have been able to distinguish between the nitrate ion and a covalently bonded nitrate group in these compounds. Addision and Gatehouse (*76, 77*) have also examined several anhydrous nitrates in this way.

Peppard and Ferraro (*78*) have applied this method to the study of the organophosphorus complexes of nitrates. They have examined the infrared spectra of the nitrate-bis-(2-ethylhexyl) phosphate complexes of M(VI) cations, and have noted the lowered symmetry in these complexes. Ferraro (*79*) studied the nature of nitrate in the TBP (tri-*n*-butyl phosphate) solvated nitrates [M(III), M(IV), and MO_2(II) type], and observed a greater lowering in nitrate symmetry in these complexes than is present in the hydrated nitrates themselves. The nature of the mineral acid (HNO_3) extracted into HDEHP (bis-(2-ethylhexyl) phosphoric acid) and TBP was also studied by this method (*80*).

The infrared spectra of several metallic nitrates were examined (*81*), and the observation made that in going from a monovalent metallic nitrate to a tetravalent metallic nitrate there is an increased lowering of the nitrate symmetry, and a transition from a point group D_{3h} symmetry to a point group C_{2v} symmetry.

The observed changes in the nitrate symmetry in inorganic nitrate compounds has proved to be very useful in giving additional information as to the nature of the nitrate present.

Carbonates. As with the nitrates, Gatehouse, *et al.* (*82*) have attributed the decrease in symmetry arising in carbonates to covalent bonding. The carbonate ion has a D_{3h} symmetry giving rise to four vibrations. When the carbonate ion is covalently bound through one or two oxygens the symmetry is lowered to that of a point group C_{2v}. The ν_3 vibration in the carbonate ion is in a doubly degenerate state and is split into two components when the carbonate ion is coordinated, ν_4 and ν_1. The following compounds illustrate the results obtained for a covalent carbonate.

	ν_4	ν_1	ν_2	ν_6	ν_3 or ν_5
[Co en CO_3] Cl	1577s	1281s	1059w		
		1272s	1035w	830s	754m
Dimethyl carbonate	1760s	1280s	969s	793s	

The basic carbonates and hydrogen carbonates also

Table 3. Frequency Ranges of Carbonate Absorption Bands (82)

Type of Carbonate	OH	ν_3 1470–1420	ν_4	ν_1 1090–1020	ν_1	ν_2 890–820	ν_2	ν_4 (cm^{-1}) 750–680 ν_6	ν_3 or ν_5
Simple									
Basic	3390–3270		1515–1470		1425–1325		1049–1047	877–835	712–686
Complex	...		1577–1493		1338–1260		1082–1055 1050–1021	889–824	809–738
Acid	3300–3200		1660–1655 1630–1620		1410–1400 1370–1295		1050–1010 1000–990	840–830	705–688
Organic	...		1870–1750		1280–1252		1021–969	793–774	...

show this splitting. Table 3 illustrates the frequency range of the carbonate absorption bands.

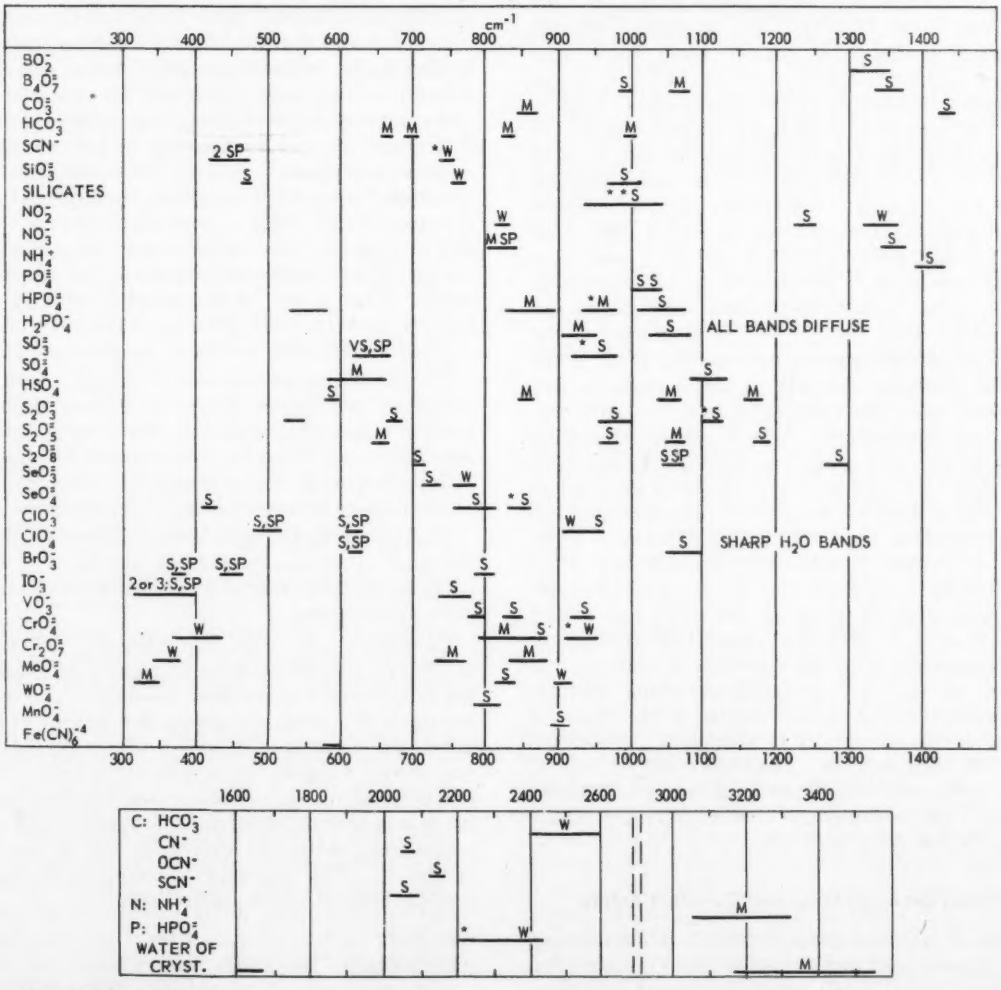
Far Infrared Spectra

A recent publication (*83*) reported on the infrared spectra of over 200 inorganic compounds in the cesium bromide region. Characteristic frequencies are listed for some inorganic ions in the cesium bromide region (300–700 cm^{-1}), and in the sodium chloride region (700–3600 cm^{-1}), in Table 4.

The Infrared Spectra of Metal-Oxygen Double Bonds

The infrared spectra of several compounds containing metal-oxygen double bonds has been reported (*84*). The results show that in compounds where one metal-oxygen double bonded link exists, an absorption occurs

Table 4. Characteristic Frequencies of Polyatomic Inorganic Ions (300–3600 cm^{-1}) (*8, 83*)



* In most, but not all, examples.
** Literature value.
S, strong; M, medium; W, weak; SP, sharp.

at 952–1087 cm^{-1}. The compounds studied in this class were $VOSO_4$, VO(acetylacetone), Ti(acetylacetone)$_2$, K_2MoOCl_5, K_2CrOCl_5, and $VOCl_3$. In compounds where two oxygens are linked to the metal (e.g., CrO_2Cl_2 and CrO_2F_2), the absorption occurs at 970–1016 cm^{-1}. In compounds where there are more than two metal-oxygen bonds (V_2O_5, CrO_3, MoO_3, $KMnO_4$, $KReO_4$, K_2CrO_4, and $K_2Cr_2O_7$), the absorption occurs at 825–1020 cm^{-1}. The absorptions in this region are of diagnostic value if no atom of similar atomic weight is present which might give frequencies in the same region.

Summary

Several examples have been discussed, which serve to illustrate the application of infrared spectroscopy to inorganic chemistry. With the availability of commercial high resolution infrared spectrophotometers, interest in inorganic infrared spectroscopy should continue to develop. The method is very useful and is certainly not restricted to organic compounds.

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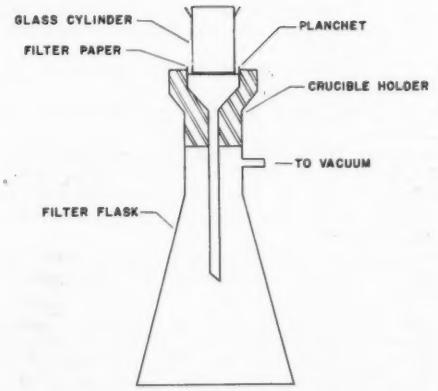
T. E. Burgess,[1] **J. T. Looby,**[2] and **W. C. Orr**
University of Connecticut
Storrs

Disposable Plastic Mounts for Radioactive Samples

Radioactive precipitates are usually mounted, for counting purposes, by suction filtration on sintered glass plates or filter paper. Both types of mounts may lead to trouble: the glass plates are difficult to clean after use; and there is a tendency for the filter paper to curl upon drying, after the filtration, which may lead to an error in geometry of the mounted sample. The following technique was developed in the U. of Conn. laboratory and has been used for some time, giving readily reproducible results.

Acrylic plastic planchets,[3] 1/4 in. deep, 1 in. in diameter, and with a 1/4 inch lip, are coated with a thin layer of an acetate base cement; then the filter holes are drilled. After the sample is collected on filter paper placed in the planchet, the suction is removed and a few drops of ethyl acetate are added to moisten the cement and paper. Suction is again applied, and the paper is neatly cemented to the planchet. The sample can be easily removed after counting if further experimental work is desired.

The apparatus shown which can be used in mounting the radioactive samples consists of a filter flask, a Gooch crucible holder, a perforated planchet, a disc of fine filter paper, a cylindrical glass tube ground flat on the bottom and having two ears attached to opposite sides of the cylinder, and an elastic band. The elastic band is attached between the ears of the cylinder and a wire wound around the Gooch holder to supply the pressure necessary to prevent leaks when the sample is filtered.



APPARATUS FOR MOUNTING RADIOACTIVE SAMPLES

Where dense solids are to be mounted, a 4-in. filter tube may be used in place of the short cylinder shown in the diagram. In this case, for a more uniform mounting geometry, first fill the tube half full of water, then add the sample mixed with water and allow the solid to settle into an even layer before applying the suction.

[1] Present address: Sprague Electric Co., North Adams, Mass.
[2] Present address: E. I. Du Pont de Nemours and Co., Inc., Newport, Del.
[3] Obtained from W. Howard Stagg, Plastic Engineering, 2113 E. Sergeant Street, Philadelphia, Pa.

Robert M. Brooker[1]
Indiana Central College
Indianapolis
and **Richard T. Rapala**[2]
Eli Lilly and Co.
Indianapolis

The National Science Fair-International and the ACS Chemistry Awards

During the 11th National Science Fair-International at Indianapolis in May, 1960, the American Chemical Society presented the "ACS Chemistry Awards" for the first time. The Society plans to continue these awards in future National Science Fairs; this paper is presented to explain the mechanics of the awards and to inform interested high school teachers and students of the basis of selecting the winners.

The National Science Fair program, sponsored by Science Service and other organizations both academic and industrial, has as its main objective inspiring greater interest among students in the fields of pure and applied science. This it does by identifying and encouraging the scientifically gifted students, by permitting the younger group to express themselves by using their skills and interest in science, and, indirectly, by reinforcing science teaching and creating a demand for better science instruction. Scientific organizations provide time, effort, and money to support this program. Many scientists, independently or through their science affiliations, give technical service and advice in the rôle of advisors to the individual exhibitors, help to organize the science fairs, and aid in the arduous task of judging the many exhibits.

Although many local sections of the ACS have been cooperating with the National Science Fair program for several years, 1960 was the first year the national organization participated. The ACS Chemistry Awards were two $100 gifts for purchase of books or equipment, one to the first place boy and one to the first place girl chemistry project winners. The first place and runner-up boys and girls were each given an inscribed plaque and a year's subscription to the JOURNAL OF CHEMICAL EDUCATION. These awards were in line with the presentations made by other national scientific organizations. The awards were presented by the ACS chairman of the local section to the winners at one of the award banquets. Each plaque was returned to the ACS representative for the purpose of engraving it with the winner's name and school, then was re-presented to the winner at a meeting of the local section of the ACS in his area. The local ceremony also included the presentation of an inscribed certificate recognizing the winner's sponsoring teacher.

The judges for these awards are selected by the ACS representative from the local and surrounding ACS sections and are persons who have not acted as judges for either a state or local science fair during the year. The four judges from four different ACS sections for the 1960 National Science Fair Chemistry Awards were eminent chemists in four different fields of chemistry: three came from universities and one from an industrial concern.

The projects to be evaluated by the judges varied from simple devices illustrating fundamental laws to complex modern equipment, from collections and data processing to sound experimental studies and interpretations. Since true chemistry encompasses so many branches it was necessary to scan all entered exhibits for possible chemical nature. In this manner then, projects that were not listed as chemistry exhibits, but could be defined in this category by the judges, were considered.

The ideas for the science projects came mainly from books and magazines, from faculty members, and from summer work. Moral as well as scientific support was constantly furnished by parents and teachers. Typically, the initial step of formulating the idea and concept was followed by a thorough library search and then by correspondence with academic and industrial scientists to concentrate the basic interests. As the plan developed and unfolded, any shortcomings in the idea or in the student which became apparent necessitated more reading, further consultation, more correspondence, and additional discussion. With the experimental work under way, the project could take a complete change of course or it could run tangent to the original concept; consultations with academic and industrial scientists were continued. The student was able to show his creative ability at the different stages of the project, in selecting the method of approach and the experimental design, in recording his observations of the expected and the unexpected, and in interpreting his results. The completed project then became one of good basic ideas, experimental studies, and well-organized data which represented for the young student a rewarding intellectual research experience. The more successful exhibits had certain characteristics apparent to the interested observer, including a clear statement of (1) the purpose of the project, (2) the method of solving the problem, (3) the recording of experimental observations, (4) the interpretation of the experimental results, and (5) the conclusions, supported by the data obtained.

According to the National Science Fair rules, the exhibits are judged on creative ability, scientific thought, thoroughness, clarity, dramatic value, and technical skill; the values range from 10 to 30 points for each part with a total point value of 100. Each chemistry project was evaluated by each of the teams of two judges. The initial screening to eliminate less than

[1] Chairman, Indiana Section, ACS, 1959–60.
[2] Chief of Judges for the ACS Chemistry Awards at the 11th National Science Fair International.

outstanding projects was based on a committee elimination rather than upon any one individual's judgment. In the final judging, originality and ability were stressed along with interest, neatness, and clarity of presentation by the exhibitor (the posters and legends which accompanied the exhibit and their explanation by the contestant were also considered). The judges were interested in the main purpose of the exhibit, the fulfillment of its objectives, the description and procedures used, the results achieved, and whether further work was needed. They were not interested in routine analyses or cookbook projects, in the building of an apparatus without making use of it in a novel way, in collections as such, or in a colorful and unusual display which demonstrated a lot of work but little scientific planning. All of the judges felt that it was necessary that the student have a deep intellectual interest in the subject as well as a knowledge of the area surrounding his particular exhibit. They wanted the exhibitor to show that he could and did think independently when preparing his exhibit. Since most of the contestants had the advice and help of one or more senior scientists, the judges spent considerable time in determining whether the student was working as an individual dependent on his own intellectual resources or was being completely directed by the sponsors.

Perhaps the greatest result of these fairs is the discovery of our most fundamental natural resource—the young men and women with the potential leadership that human society requires for continued existence in a world of change. To keep America strong we must constantly advance our technological progress; we know that to these students will fall the responsibilities for our scientific, industrial, and cultural advancement and the future of this nation.

Reviews of ACS Cooperative Exams

Qualitative Analysis, Form 1960

The new Qualitative Analysis Examination, Form 1960, consists of three parts:

I. Recall of information and balancing of equations, 20 items, 20 points, 25 minutes time allowed;
II. Qualitative application of principles, 30 items, 60 points, 50 minutes time allowed;
III. Quantitative application of principles ("problems"), 10 items, 20 points, 30 minutes time allowed.

This test excels in a number of ways, some of which indicate progress compared with previous forms; e.g., the student is told how much credit each part carries, so he can distribute his efforts wisely. Total credit adds up to 100 points, making the scores immediately comparable with those of other tests given on that same basis. The total number of items was reduced from 80 to 60, and the time allowed to answer them was increased from 100 to 105 minutes. Time, therefore, is not the limiting factor any more, and a good student may be expected to get the whole test done and to achieve a score of 90 to 100 points.

The material covered in the test offers a rather complete cross section of the knowledge and the abilities expected at the end of a qualitative analysis course. The balance of subjects could perhaps be improved in future editions by reducing somewhat the number of questions dealing with ammino complexes, amphoterism, and hydroxide precipitation (about 20% now).

The phrasing of the questions is simple, clear, and unambiguous, and the answers to choose from are so carefully worded that they do not lead, and a multiple choice really exists. In this respect the test is so well done that it may help some of the instructors who do not really like multiple choice tests become reconciled to the ever-mounting necessity to save time by using them.

The problems in part III, testing for comprehension of the laws and correct setting-up of equations, avoid lengthy arithmetic. The slide rule, the use of which is permitted, will not be very busy.

Since the emphasis of the whole examination is strongly on the intelligent application of principles, the test may also be used to advantage in qualification exams of new graduate students, preferably in combination with a few essay type questions on more advanced concepts.

Richard E. Frank
University of North Dakota
Grand Forks

General Chemistry, Form 1960

This latest test in General Chemistry conforms to the traditional pattern:

I. Recall of information, 30 items, 30 points, 20 minutes time allowed;
II. Application of principles, 45 items, 45 points, 50 minutes time allowed;
III. Quantitative application of principles, 25 items, 25 points, 35 minutes allowed.

The periodic table and atomic structure receive the greatest emphasis, followed by chemical bonding, equation balancing, and kinetic molecular theory. The remainder of the test affords a well-balanced coverage of the most important topics in the first year course in which organic chemistry is deemphasized.

The trend in teaching general chemistry is away from encyclopedic treatment of descriptive chemistry toward an emphasis on concepts for interpretation and predictions. In this respect, it is gratifying that in this examination the recall primarily concerns tools for reasoning in chemistry.

Several of the questions in Part II more appropriately belong in Part I, because the correct answers given among the choices are too obvious to require application of principles. Students should be required to extract some information from a graph; unfortunately, the correct answer to the single problem of this type can be ascertained without use of the graphic data, a phase diagram. "None of these" is offered as a choice only twice; more frequent use would be desirable. It is commendable that reading skill, as well as proficiency in chemistry, is required to answer a few questions.

Form 1960 is printed in attractive, easily read type, a tremendous improvement over older examinations. The norms accompanying the test permit versatile use of the results for comparative evaluations: the sample is large (3506); sub-groups within the sample are well classified.

The test would not be an adequate challenge to students in a rigorous honors course. It is, however, an improvement over older examinations and is satisfactory for use with other general chemistry classes.

S. L. Burson, Jr.
Pfeiffer College
Misenheimer, North Carolina

Division of CHEMICAL EDUCATION
American Chemical Society

Condensed Norms: ACS Cooperative Examinations

Two new tests were released in the spring of 1960, General Chemistry 1960 and Qualitative Analysis Form 1960.[1] The norms on these tests have been calculated from the reports, and a condensed version is given below.

The condensed norms are selected from a much larger body of data which can be obtained from the Examinations Committee, American Chemical Society, Theo. A. Ashford, Chairman, University of South Florida, Tampa 4, Florida.

QUALITATIVE ANALYSIS, FORM 1960

Maximum possible score	Sub groups SC[a] 100	Sub groups QG[b] 100	Entire group[c] 100
Percentile rank			
99	91.0	96.2	95.6
95	86.3	88.2	88.0
90	79.5	82.4	81.7
85	74.0	78.1	77.5
80	70.1	73.8	72.2
75	67.1	69.4	68.4
70	63.5	64.7	64.5
65	59.9	61.4	60.9
60	55.3	57.9	57.6
55	53.1	53.1	53.1
50	50.5	49.0	49.8
45	48.1	45.7	46.4
40	44.5	42.8	43.4
35	43.0	39.7	40.7
30	40.5	36.7	37.3
25	36.6	32.3	34.0
20	33.3	29.2	30.3
15	30.2	22.2	25.4
10	26.5	18.2	20.1
5	18.3	11.7	13.6
1	6.6	4.8	5.6
Reliability Coefficient	0.958	0.976	0.971

The scoring formula used was R-W/4 throughout.
The figures given are raw scores.
The reliability coefficient was estimated by the Kuder-Richardson Formula No. 21.

[a] The SC group consists of 210 students in 6 institutions, taking a *separate course* (one semester or one quarter) in Qualitative Analysis.

At the end of the course the students received 3.5–5 credit hours, the mean being 3.9. In all six schools there were 2–3 lecture hours per week with a mean of 2.3 and from 3–8 laboratory hours per week with a mean of 4.4.

[b] The QG group consists of 534 students in 8 institutions taking the Qualitative Analysis as a part of General Chemistry in the second semester of the latter.

At the end of the second semester of this course, the students received 4–5 credits, the mean being 4.6. There were 3–4 lectures per week, the mean being 3.1. There were 3–6 laboratory hours per week with a mean of 3.8.

[c] The entire group consisted of 744 students in 14 institutions, and is the sum of groups SC and QG above. The characteristics of the total group are substantially the same as the large QG group above.

[1] Condensed norms for the currently used ACS Cooperative Examinations have appeared in THIS JOURNAL, **34,** 144 (1957), **35,** 244 (1958); **36,** 148 (1959); **37,** 166 (1960).

GENERAL CHEMISTRY, FORM 1960

Maximum possible score	Sub groups Q[a] 100	Sub groups N–Q[b] 100	Entire group[c] 100
Percentile rank			
99	83.5	86.7	85.7
95	75.9	72.6	75.0
90	70.1	65.4	68.4
85	66.0	60.7	63.9
80	62.2	56.8	59.8
75	58.8	53.9	56.4
70	55.5	50.6	53.4
65	52.5	47.2	50.3
60	49.7	44.6	47.8
55	47.7	42.1	45.6
50	45.7	40.4	43.3
45	43.5	37.5	41.0
40	41.2	35.6	38.6
35	38.9	33.2	36.5
30	36.9	31.1	34.1
25	34.3	28.7	31.6
20	31.6	26.0	28.9
15	28.3	23.8	26.1
10	25.1	19.9	22.7
5	19.3	15.2	17.4
1	13.6	7.5	10.2
Reliability coefficient	0.935	0.938	0.937

The scoring formula used was R-W/4 throughout.
The figures given are raw scores.
The reliability coefficient was estimated by the Kuder-Richardson Formula No. 21.

[a] A sample of 1751 papers from 20 institutions was selected from the entire group with fairly common characteristics.

The students were tested at the end of a two-semester course receiving 8–10 hours credit, the mean being 8.8. In all schools there were 2 to 4 lecture hours per week, with a mean of 3.0 and from 3–6 laboratory hours per week, with a mean of 4.3. Several weeks of Qualitative Analysis were taught to these students, ranging from 11–18 weeks, with a mean of 13.8 weeks.

[b] A sample of 1563 papers from 19 institutions was selected from the entire group with fairly common characteristics.

The students were tested at the end of a two-semester course receiving 8–10 hours credit, the mean being 8.5. There were 2–3 lecture hours given per week, with a mean of 2.9 and 1–4 laboratory hours per week, with a mean of 2.8. Little or no Qualitative Analysis was taught, the range being from 0–7 weeks with a mean of 3.8 weeks.

[c] The entire group totaled 3506 students from 41 institutions.

All students were tested at the end of a two-semester course receiving credit varying from 6–10 hours with a mean of 8.6 hours. In these schools the lecture hours per week ranged from 2–4, the mean being 2.9 and the laboratory hours from 1–6 hours per week, with a mean of 3.6. There was a wide range of total weeks spent on Qualitative Analysis, ranging from 0–18, with a mean of 9.0.

Proceedings of the

California Association of Chemistry Teachers

Robert L. Pecsok
University of California
Los Angeles

Gas Chromatography

Basic principles and new developments

Seldom in the history of chemistry has an instrumental technique attracted so much immediate attention as gas chromatography. In the brief span of time since 1952 when James and Martin published a method for the separation and micro-estimation of volatile fatty acids by gas chromatography (*1*), the literature has expanded at an exponential rate. Currently, about 30 papers are abstracted each week (*2*). Nearly every technical meeting features a session on new developments.

Gas chromatographs are already monitoring and controlling major processes in industry (*3*). The technique has revolutionized much research in organic chemistry: gasoline samples have been separated into 125 components (*4*); the smoke from a single puff of a cigarette (*5*), insecticide residues (*6*), the aroma of a can of coffee (*7*), the flavor of a strawberry (*8*), all can be analyzed by this powerful technique. Isomers of long chain fatty acids differing only by the position of a double bond can be distinguished. Sample sizes have been decreased to small fractions of a microliter and increased to tens of milliliters. The speed of analyses has increased to the point where multicomponent mixtures can be separated in few seconds and recording potentiometers are no longer fast enough to tell one how good the separation was—oscilloscopes must be used (*9*).

Clearly, this is a subject which we must teach, and yet it is so new that few of the standard instrumental textbooks give more than a brief indication of its importance. One of the reasons for this situation is that hardly any of the major contributions have come from American University laboratories. Until recently, the leaders in the field were to be found in England, Holland, Sweden, Czechoslavakia, and Russia. Most of the important ideas have come from biochemical laboratories, petroleum research laboratories, and instrument companies. Another reason why applications have outdistanced an understanding of fundamental principles is that the technique is so simple and inexpensive that thousands of chemists are now using it as an indispensable tool after reading a few papers and perhaps the instruction manual. But in order to choose components wisely, realize the ultimate in performance, and achieve the fantastic results that are now possible, it is essential to acquire a sound knowledge of fundamental principles.

Presented at the Summer Conference of the CACT, Asilomar, California, September, 1960.

Numerous reviews (*10, 11, 11a*) and several monographs (*12, 13, 14*) on gas chromatography are available for detailed study. The purpose of this paper is to present a brief introduction to the principles and a look at current developments in this fast moving field. We shall consider only gas-liquid elution chromatography. For a more general elementary discussion, the article by Lotz and Willingham (*15*) is very useful.

Principles

Gas chromatography, like all chromatographic methods, is primarily a technique for performing separations. Many separations, such as the precipitation of silver chloride or the extraction of iron(III) chloride from water into isopropyl ether, are essentially quantitative in a single step. Other more difficult problems, such as the separation of *o*- and *p*-xylene with very similar physical and chemical properties, may require thousands of steps; the thousands of steps are readily attained in a simple chromatographic column requiring essentially no labor on the part of the operator.

All chromatographic methods involve a stationary phase which partially adsorbs or absorbs the sample components and a moving phase to transport the sample components along the column or across the medium. The components tend to equilibrate between the two phases and are moved only during the fraction of time spent in the moving phase. Thus the average rate of movement is determined by linear velocity of the moving phase and the distribution coefficient, and will, of course, be different for each component. The peculiar advantage of gas-liquid partition chromatography lies in the fact that we can take advantage not only of physical properties such as vapor pressure, but also of chemical properties such as complex formation, hydrogen bonding, molecular dipole effects, etc. The only requirement is that these chemical reactions be reversible under the conditions extant in the column.

Under ideal circumstances, we would expect that if the column is long enough each component would emerge at a different time as a very narrow band, making difficult separations easy. The chromatogram would consist of a series of sharp spikes, a dream of all chromatographers. Actually, even a sample consisting of only one pure component inevitably spreads out as it passes through the column, and becomes broader the more time it spends in the column, obviously complicating the picture and making separations more difficult. It is this phenomenon of "band broadening"

that has given rise to several theories attempting to explain it. The important objective is to understand the reasons for band broadening in order to maintain as narrow a band as possible.

Martin and Synge (*16*) proposed an explanation based on "theoretical plates," analogous to multistage separations. A column can be considered as consisting of a large number of discrete stages or plates, in each of which equilibrium between the phases is established before the mobile phase moves to the next plate. With this model one can predict the distribution of a component after a given number of transfers. For example, let us assume a distribution coefficient of unity (equal concentrations in the gas and liquid phases) and equal volumes of each phase in each plate. We then introduce a component to the first plate, establish equilibrium, and transfer the moving phase to the next plate. The component is introduced to the system only once, and after each transfer the system is replenished with a volume of pure carrier entering the first plate. With this scheme of operation, after the first transfer, one-half the component is in the first plate and one-half in the second. The next transfer moves one-quarter of the component into the third plate, one-quarter remains in the first plate, and one-half (but not the same half) remains in the second. If this process is repeated many times, the fraction remaining in each plate is obtained from the values of the successive terms of the binomial expansion $(a + b)^p$, where p is the number of the last plate used and a and b are both equal to $^1/_2$. More generally, the distribution coefficient, K, will not be unity, and the volumes of the phases, V_G and V_L, will not be equal. The distribution (the fraction of the component in each plate) among the plates is then obtained from the expansion of the expression:

$$\left(\frac{1}{E+1} + \frac{E}{E+1}\right)^p, \text{ where } E = \frac{V_G}{KV_L}$$

A distribution of a typical component after 10 and 20 transfers is shown in Figure 1. From these considerations alone, it would appear that the use of more plates (or transfers) spreads out the material over a broader band. It also appears that separations are impossible since one can never remove all of the material from the first plate. The answer to this apparent dilemma is to decrease the size of each plate.

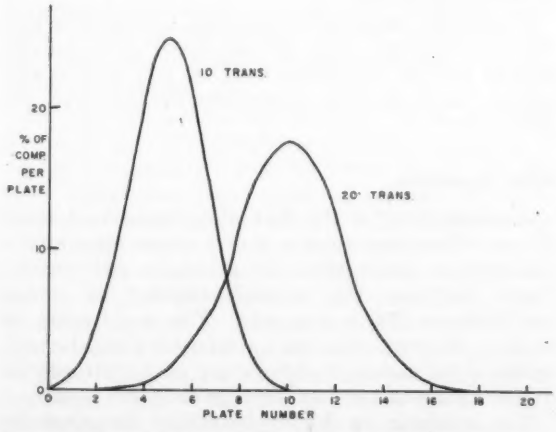


Figure 1. Distribution of a component after 10 and 20 transfers.

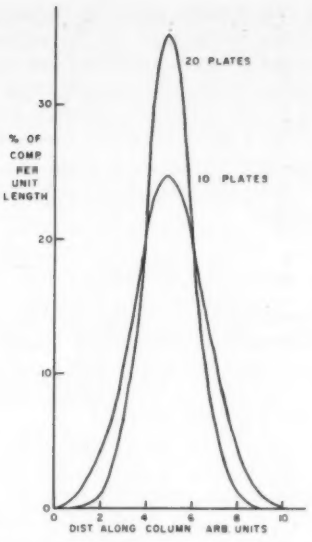


Figure 2. Distribution of a component in two columns of equal length but containing 10 and 20 plates.

For example, let us reconsider the distribution of material depicted in Figure 1, on the basis of unit of column length rather than unit plate. This same distribution is replotted in Figure 2, for two columns of identical length, but containing 10 and 20 plates, respectively. It is obvious that the column with the greater number of plates approaches our ideal picture more closely. As the number of plates is increased, the component occupies a larger number of plates, but most of the component is located in a small fraction of this large number. Thousands of plates are common in gas chromatography and sharp peaks are readily obtained.

The distributions shown in Figure 2 are for a single instant when the first part of the sample just reaches the column exit, and the maximum concentration is in the center plate. The distribution with time is shown in Figure 3, where it is seen that the peak inevitably broadens as it passes down a column. In

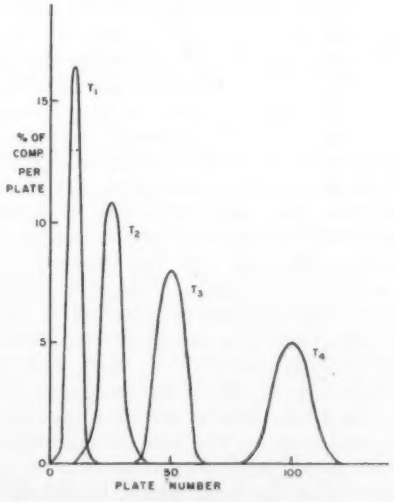


Figure 3. Distribution of a component at various times.

practice, one can observe only the instantaneous concentration of the component in the carrier gas as it emerges from the column, and from this one infers the prior distribution within the column and the number of plates that would have been required to achieve this curve. Thus, in a practical sense, one determines the number of theoretical plates, n, from the distribution curve (rather than the reverse process outlined above) using the formula:

$$n = 16(t_R/w)^2$$

where the retention time, t_R, is the time required to reach the maximum concentration (peak) of a component and w is the band width, measured in time units between the intersections of tangents to the inflection points of the peak and the base line.

While the number of theoretical plates gives us a measure of the column performance (efficiency), it tells us nothing about what determines it or how to improve it, except to add more plates (make a longer column). Actually we would prefer to build more plates into the same length of column. The most useful attempt to explain the effect of experimental parameters on the height equivalent to a theoretical plate, H, was proposed by Van Deemter (*17*). He considered "band broadening" kinetically and suggested a rate theory. Obviously, in a continuously moving system equilibrium can be approached but never established. There are other deviations from ideality. The distribution coefficient is not a constant, but depends on the total concentration (although nearly constant for liquid stationary phases). The liquid phase is not uniformly distributed throughout the column. The molecules in the gas phase move along devious paths of non-uniform lengths. In addition to convection, there is linear diffusion along the column in both phases. An exact theory accounting for everything would be unnecessarily complicated. Van Deemter (*17*) proposed that three terms were sufficient to account for H in a simple fashion:

$$H = A + B/u + Cu$$

where u is the linear gas velocity. The A term is a measure of the path variation and increases with the size of the solid particles. The B term is a measure of linear diffusion along the column in the gas phase; it increases with the gas diffusivity and decreases with the gas velocity (less time spent in the column). The C term is a measure of the resistance to mass transfer (departure from equilibrium), and depends on the actual value of the distribution coefficient, the thickness of the liquid film, the liquid diffusivity, and, of course, it increases with the gas velocity (less time to reach equilibrium). Although the Van Deemter equation appears to give the height equivalent to a theoretical plate, it is rarely possible to calculate H from this equation alone because it includes terms which cannot be experimentally measured. It does, however, predict the effect of many parameters on column efficiency.

There have been several recent proposals (*18–20*) to modify and improve the Van Deemter equation by adding additional terms to account for the effect of linear diffusion in the liquid phase, lateral diffusion in the gas phase, adsorption on active sites of the solid support, relatively stagnant areas of gas, and adsorption on the surface of the liquid. These refinements add complications in the application of theory, but are necessary for highest efficiency.

Despite the shortcomings of the Martin-Synge and the Van Deemter theories, they have been of enormous value in developing better columns. The work of Golay (*21*) is an outstanding example of the rewards of this sound approach. By considering the Van Deemter equation, he correctly reasoned that regardless of how the column is operated, the value of H can never be reduced to less than the value of the A term which is determined by the tortuous path through the irregular packing material. To eliminate this limiting factor, he suggested that an empty capillary column, coated with liquid phase, would approach an ideal situation. He was able to predict from mathematical arguments the optimum diameter of such a capillary. Capillary columns now in use with internal diameters of about 0.01 inch and lengths of several hundreds of feet give a phenomenal number of theoretical plates; up to a million plates has been reported (*22*).

The initial excitement suggesting that capillary columns would make packed columns obsolete has subsided. One must pay for a million plates in terms of increased retention times and smaller capacity. A sample of a fraction of a microgram may be highly desirable if this is all that can be obtained, but for most applications such a small sample is difficult to measure and handle. Furthermore, recent work has shown that the number of plates is a somewhat misleading measure of the performance of a capillary column; in fact it may require up to a hundred times as many plates to perform a given separation in a capillary as in a small packed column (*23*).

The practicing chromatographer is more interested in performance than in theoretical numbers. In addition to column efficiency measured in plates, the resolution of two components depends to a large extent on the nature of the stationary phase. Two components with overlapping peaks can be separated by sharpening the peaks (increasing the number of plates), by changing the relative rates of movement through the column (employing a liquid with a more favorable differential between the two distribution coefficients), or by an appropriate combination of both factors (*24*). Purnell (*23*) has given an excellent correlation of separating power and efficiency.

For process control and other applications where high speed is essential, both factors must be considered. This is an area of intense activity, and several suggestions are available for minimizing the time (*11a*, *25–27*).

New Apparatus

Although many of the applications mentioned above require refined instruments, a very simple apparatus is sufficient to demonstrate the principles and perform simple analyses. The version suggested by Cowan and Sugihara (*28*) is adequate. This could easily be used by students, although for safety it would be preferable to use carbon dioxide rather than hydrogen for a carrier gas with a nitrometer-type detector (*29*, *30*).

The emphasis on higher sensitivity (required for trace constituents and small samples) has increased

the demand for ionization detectors in which the components are ionized by β-rays (*31, 32*), flame temperature (*33, 34*), or thermal electrons (*35, 36*). With these detectors it is possible to measure amounts as small as 10^{-15} g of material. The extremely small ion currents observed require tremendous amplification; however, this has been achieved with electrometers giving linear response over ranges of 5 to 7 orders of magnitude (*37*). In general they are less sensitive to temperature fluctuations. The three varieties are more or less equivalent for many applications. On the other hand the flame detector is insensitive to water and other non-combustible gases, and of course, the components are destroyed. The β-ray detector is relatively insensitive to low molecular weight substances, and requires a radioactive source. The thermal ionization detector is more generally applicable but the current models do not possess the extreme sensitivity of the other two. The thermal conductivity detector remains the most popular choice because of its low cost, simplicity, and wide applicability. Miniature thermal conductivity detectors are now approaching the sensitivity of ionization detectors (*38*). A new version (*39, 39a*) of the Martin gas density balance is now available. This detector responds directly to molecular weight, thus eliminating the problem of calibration.

It will not be long before everything in the stockroom has been tried as a stationary phase. The use of Tide from the grocery store has proved very effective (*28, 40*). Modifying the solid support with a thin layer of hexamethyldisilazane has lessened the tailing problem with polar compounds (*41*). Granulated Teflon will do the same (*42*). Thin layers of silicone (General Electric SE 30) have made possible the separation of steroids and alkaloids far below their normal boiling points (*43*). In general, resolution is improved at lower temperatures, and an interesting new material has been prepared at the Naval Ordnance Test Station (*44*) called 1-methyl (2-ethylhydroxy) tetrazole which remains as a supercooled liquid at temperatures as low as −190°. It is reported to give excellent resolution for the fixed gases.

Micro-glass beads as a support are receiving much attention (*45*). The glass surface is far less active than diatomaceous earth so that thinner layers of liquid can be used; this tends to increase efficiency and speed and makes possible the use of lower temperatures. However the smaller specific surface of the spherical beads is a disadvantage, reducing both efficiency and capacity.

Temperature control is a limiting factor in quantitative analysis. Peak height is a sensitive function of column temperature for all detectors, and of the detector temperature for thermal conductivity detectors. Peak areas are less sensitive to column temperatures as long as the detector temperature is constant.

If the peak area is used, the column temperature need not be constant and can be programmed (*46*). Only the detector need be held at constant temperature; this is an enormous advantage for wide boiling range samples. Low boiling components are analyzed at low temperature where good resolution can be maintained and the high boiling components are gradually speeded up to give a reasonable retention time. An additional advantage is that all peaks tend to have nearly the same width. A very convincing example of the value of programmed temperature is shown in Figure 4. The theoretical treatment of this technique is extremely complicated but progress has been made (*47–49*).

High temperature work is limited only by the thermal stability of the materials and the volatility of the liquid phase (*50*). Organic materials (e.g., silicones, Apiezon greases, asphaltenes, etc.) are useful to about 350° (*51*); above this temperature one must resort to inorganic salt eutectics (*52*). Some work has already been done up to 500–600°, and 1000° seems attainable shortly.

Gas chromatography is essentially a micromethod requiring small diameter columns and small samples. Furthermore elution chromatography, which is the most potent separating technique, is inherently a batch process. It is a great pity that we cannot easily scale up the apparatus and make use of the method for the preparation of large quantities of difficultly purified chemicals (*53*). Preparative scale chromatographs are available, but continuous elution chromatography has not yet been achieved.

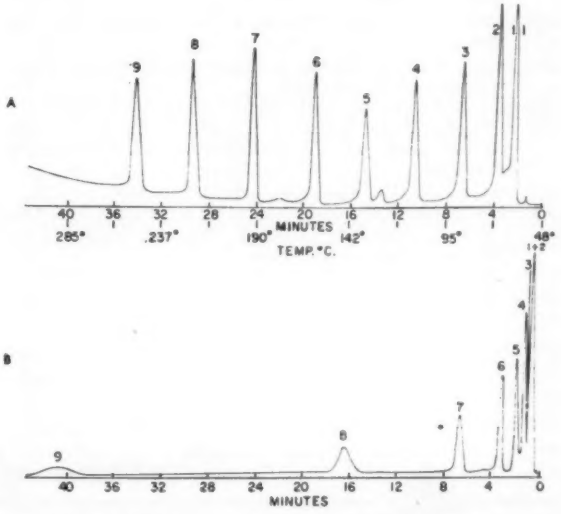


Figure 4. Gas chromatograms of alcohols. Top, programmed temperature. Bottom, constant temperature, 165°C. [Reprinted from *Analytical Chemistry*, 30, 1158 (1958).]

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A battery of tests to be used by graduate schools for placement of entering graduate students is currently under construction and should be available by autumn, 1961. The battery will include a 90 minute test in each of the fields of analytical, organic and physical chemistry. Further inquiries regarding this battery should be addressed to Dr. Harry G. Day, Indiana University, Bloomington, Indiana.

Report of the New England Association of Chemistry Teachers

Jay S. Roth
The University of Connecticut
Storrs

Ribonucleic Acid and Protein Synthesis

The exact arrangement of the amino acids in three relatively simple proteins has been determined. These proteins are the hormone insulin, the enzyme ribonuclease, and the unit protein of tobacco mosaic virus. If we examine the arrangement of amino acids in these proteins, (insulin is illustrated in Fig. 1) it is readily apparent that the sequence is quite random, and no evidence can be found for frequently repeating simple or complex groups of amino acids.

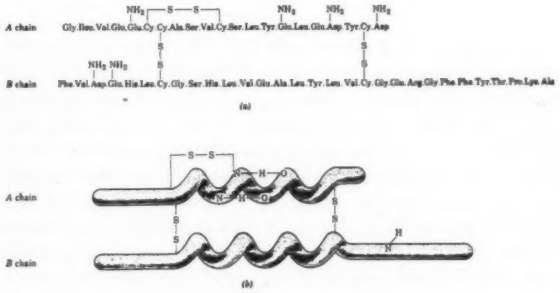

Figure 1. The structure of insulin (a) and a schematic drawing of how insulin might be coiled within the portion of the molecule which is stabilized by disulfide bridges (b). Hydrogen atoms involved in bonding between amide groups within this region might be expected to be in much slower equilibrium with the hydrogen atoms of water molecules than those in the free "tails." [From Ryle, A. P., Sanger, F., Smith, L. F., and Kitai, R., *The Biochemistry Journal*, 60, 541 (1955)].

The problem that this random arrangement poses for protein synthesis is formidable. In the course of the lifetime of a simple organism, thousands to millions of exact copies of many proteins must be synthesized. In a more complex organism, such as man, millions to trillions of identical copies must be made over the course of a lifetime.

Since approximately 20 different amino acids are found in proteins, the mechanism of protein synthesis must account for the arrangement of these 20 building blocks into the random, but highly specific, alignment characteristic of the particular protein being synthesized. A small error, such as replacement of a single amino acid (of perhaps 100 to 200 or more units) by another, may give rise to a protein which has either no functional activity or one which has abnormal activity. An interesting example of this has been observed in the case of hemoglobin S, which differs from normal hemoglobin by having a single valine unit in place of a single glutamic acid unit. Because of this, the physical and chemical properties of hemoglobin S are considerably different from those of normal hemoglobin, and these changed properties may give rise to a disease called sickle cell anemia, characterized by the formation of sickle shaped red blood cells. Although this disease in its mildest forms may not cause great difficulties, in its more severe manifestations it may lead to extreme anemia and death.

In addition to the exact sequence of amino acids in the polypeptide chain of proteins, this chain is usually folded and arranged in an extremely specific three-dimensional structure. The biological activity of the protein usually depends, to a large measure, on this three-dimensional arrangement. It has been suggested that the three-dimensional structure may actually be determined by the amino acid arrangement, because folding of the peptide chain is in turn dependent on the formation of secondary linkages within the protein. These linkages hold the protein together in the exact configuration necessary for biological activity. Among the most important of the bonds holding proteins in their specific shape are disulfide, electrostatic, and hydrogen bonds. Hydrogen bonds and electrostatic bonds as well as some other secondary bonds are illustrated in Figure 2, while disulfide bonds may be seen holding together polypeptide chains in insulin in Figure 1.

A system likely to produce identical copies is one in which a pattern or matrix serves to line up, orient, and join together the amino acids comprising the protein structure. Although a completed protein molecule immediately suggests itself as a potential matrix, there is little or no evidence that protein serves as its own blueprint.

Role of Nucleic Acids

It is now believed by a majority of investigators that nucleic acids serve as the matrices for protein synthesis. Of the two types of nucleic acid found in the

Presented before the New England Association of Chemistry Teachers Conference, Orono, Maine, August, 1960.

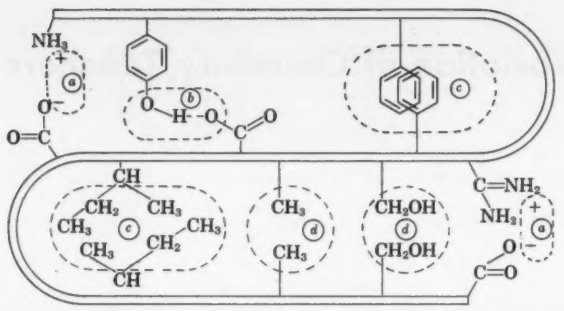

Figure 2. Some types of noncovalent bonds which stabilize protein structure: (a) Electrostatic interaction; (b) hydrogen bonding between tyrosine residues and carboxylate groups on side chains; (c) interaction of nonpolar side chains caused by the mutual repulsion of solvent; (d) van der Waals interactions. (From Anfinsen, C. B., "The Molecular Basis of Evolution," John Wiley & Sons, New York, 1959.)

cell, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA), the DNA is considered to be the master pattern, while RNA serves as the working matrix. The situation is similar to that involved in making records. A master impression (corresponding to DNA) serves to turn out thousands of like impressions. or records (corresponding to RNA). These in turn reproduce the special musical pattern (in this case corresponding to the special protein pattern) and the number of musical copies is limited only by the relative wearing quality of the record.

The actual mechanism of protein synthesis is becoming much more clearly understood on a chemical and molecular basis, due largely to the contributions of many groups of investigators, including Zamecnik, Meister, Hoagland, Berg, Schweet, Campbell, Greengard, Lipmann, and their associates.

The process of protein synthesis as it is presently visualized may be conveniently divided into the five steps which follow:

Activation of Amino Acids

The building blocks of proteins, the amino acids, are activated by an enzymic reaction which is illustrated for a typical amino acid in Figure 3.

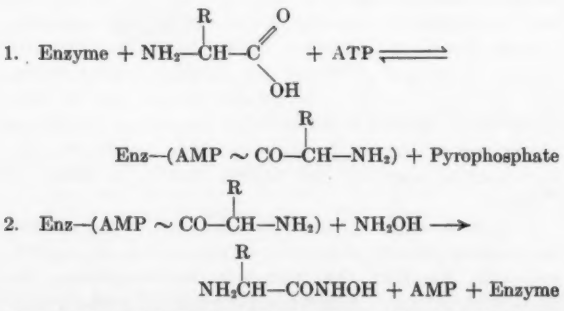

Figure 3. A postulated mechanism for the activation of amino acids for protein synthesis. In step 1 the amino acid is converted to an enzyme-bound acyl phosphate derivative of adenylic acid (AMP). This complex may be utilized for intracellular protein synthesis or, as shown in the figure, may be reacted with hydroxylamine to yield the amino acid hydroxamate.

Adenosine-5′-triphosphate (ATP), illustrated in Figure 4, combines with the amino acid to form an amino acid adenylate, which is an acid anhydride, an extremely reactive substance. Many amino acid adenylates have been prepared synthetically. They will react with almost any protein, often reacting more readily with heated, biologically inactive protein, than with native protein. They attach amino acids to free amino groups in the protein, as well as to other reactive groups present. This behavior cast doubt on the actual participation of such anhydrides in protein synthesis; but it was shown later that when an amino acid is activated, it becomes firmly bound to the activating enzyme (see Fig. 3), and when bound in this manner it is no longer as active as a free amino acid adenylate. The bound amino acid adenylate may then react at the proper place and time, in the next step of protein synthesis.

Amino acid activating enzymes have been extensively studied in rat liver where they are located in the soluble portion of the cells. They may be precipitated by adjustment of this cellular fraction to *p*H 5, hence they have been referred to as *p*H 5 enzymes.

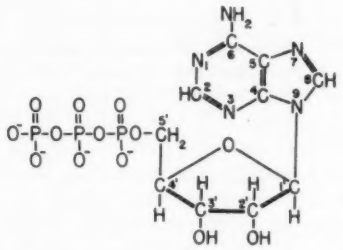

Figure 4. Adenosine-5′-triphosphate.

It appears that there may be a separate activating enzyme for each amino acid. Thus far, however, good evidence has been obtained for the existence of only about a dozen in mammalian liver. Activating enzymes for some common amino acids like glycine have not yet been detected in this tissue. It is possible that such an enzyme has low stability, or perhaps the activation process for glycine is different from the mechanism illustrated in Figure 3. Several activating enzymes have been prepared in a greatly purified state and their properties have been studied.

Addition of Nucleotide End Groups to Transfer RNA

An important substance in the protein synthetic mechanism is a low molecular weight RNA, also found in the soluble portion of the cell. (It is often referred to as "soluble RNA," but a better name that is coming into common usage is "transfer RNA.") This RNA, which has a molecular weight of 10,000–30,000, apparently occurs in the free state and not as a complex with protein. It thus differs from other types of cellular RNA which are always found associated with protein in the form of ribonucleoprotein.

Transfer RNA is best prepared by extraction of the soluble fraction of rat liver with 90% phenol. An excellent source of transfer RNA is yeast, and if intact yeast cells are shaken with 90% phenol, transfer RNA will be extracted from the yeast through the cell membranes, without rupture of the cell wall. In this way large amounts of quite pure transfer RNA may be obtained.

Transfer RNA contains large amounts of some uncommon nucleotides. Its composition with respect to

some of these nucleotides is given in Table I below, and is compared to a higher molecular weight RNA obtained from the microsome fraction of rat liver.

Table 1.

Nucleotide base	Rat liver transfer RNA (as % of related purine or pyrimidine base)	Rat liver microsomal RNA (as % of related purine or pyrimidine base)
5-Methyl cytosine	10.0	0.4
6-Methylaminopurine	8.1	0.5
6-Dimethylaminopurine	0.1	0.1
1-Methyl guanine	3.3	0.1
2-Methylamino-6-hydroxypurine	2.3	0.1
2-Dimethylamino-6-hydroxypurine	2.9	0.1
5-Ribosyluracil	25.0	7.5

Figure 5 illustrates the structures of the two purine and two pyrimidine bases which account for most of the composition of RNA. Nucleosides are formed from

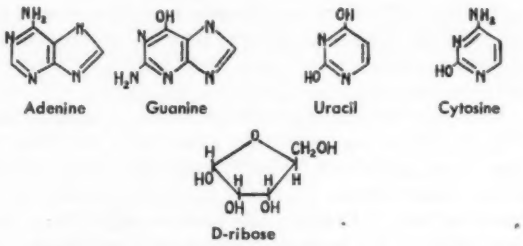

Figure 5. Components of Ribonucleic Acid (RNA).

these bases by attachment of D-ribose to the number 9 nitrogen of the purines and the number 3 nitrogen of the pyrimidines and the corresponding nucleotides have a phosphate ester at the number 2′, 3′, or 5′, on the ribose. Di- and triphosphates may also be formed as illustrated in Figure 4. In Figure 6, the structure of some of the uncommon purines listed in Table 1 are illustrated.

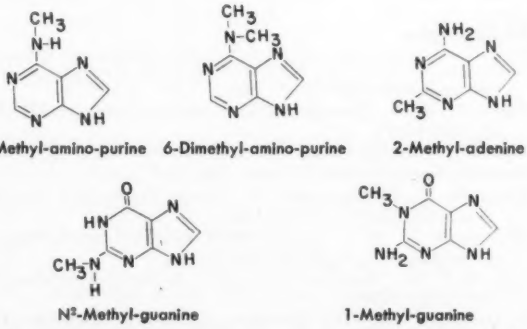

Figure 6. Structures of some trace purines from nucleic acids.

It has been determined that the nucleoside end of transfer RNA may be any of the four common nucleotides formed from adenine, guanine, cytosine, or uracil, but the other end is guanylic acid.

In order to react with the amino acid adenylate-enzyme complexes, the transfer RNA must be preconditioned first by treatment with cytosine triphosphate (CTP). Two units of the nucleotide add on to the end of the chain as illustrated in Figure 7, *a* and *b*. This is probably an enzyme catalyzed reaction. Then adenosine triphosphate (ATP) furnishes adenosine which is attached to the terminal position, Figure 7 *c;* and the transfer RNA is now ready to accept an amino acid.

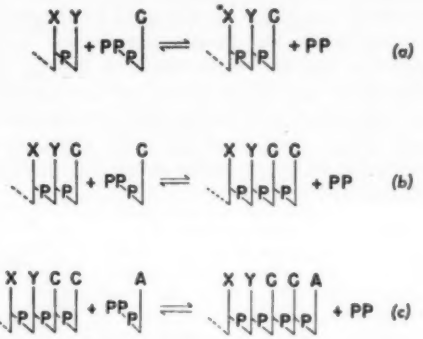

Figure 7. Terminal nucleotide additions to transfer RNA. C = cyticylic acid; A = adenylic acid.

Transfer of Amino Acid from Amino Acid-Adenylate Complex to Transfer RNA

A specificity relationship between the activating enzyme and transfer RNA exists; each amino acid activating enzyme reacts only with its particular transfer RNA, passing the activated amino acid to it. Thus the presence or absence of other amino acids has no effect, for example, on the transfer of leucine from its activating enzyme to its transfer RNA.

The amino acid appears to be bound in an ester linkage to one of the two free hydroxyls on the terminal adenosine of the transfer RNA, as illustrated in Figure 8. It is not known which hydroxyl is involved.

A protein that catalyzes this transfer of amino acids from the activating enzyme to RNA has been isolated from the soluble portion of the cell. It has also been shown that certain sulfhydryl containing compounds, particularly glutathione, may replace (in whole or in part) this protein factor.

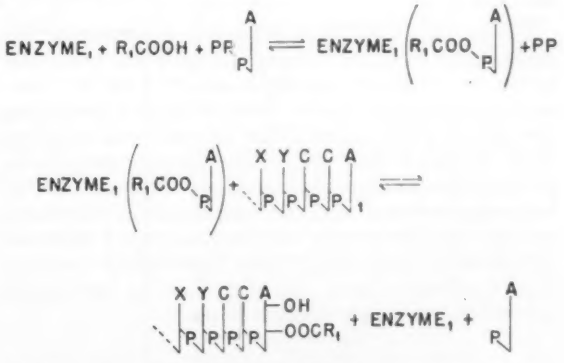

Figure 8. Amino acid attachment to transfer RNA.

Transfer of Amino Acid from Transfer RNA to Ribosomes

The ribosomes are ribonucleoprotein particles, 150–200 Angstrom units in diameter, found widely distributed throughout most cells. The RNA of ribosomes has been extracted by mild procedures using 90% phenol and shown to be of fairly high molecular weight,

possibly ranging up to 1,300,000. It is this high molecular weight RNA that is believed to serve as the pattern, or matrix, for the formation of protein; the manner in which it may do this is shown in Figure 9. This hypothetical depiction illustrates some transfer RNA molecules, each with its specific amino acid attached. The transfer RNA fits into the matrix RNA in the correct sequence by virtue of hydrogen bonding that occurs when the proper purine and pyrimidine base pairs on the two types of RNA line up together.

It should be emphasized that our knowledge of this step is fragmentary and the diagram illustrated has been deduced rather than established by experimentation. Necessary for this step is the nucleotide guanosine triphosphate (GTP).

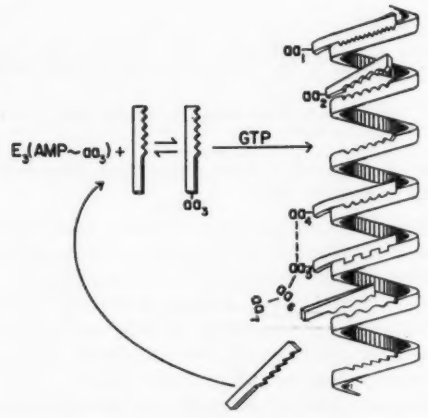

Figure 9. A schematic representation of the "adaptor hypothesis." The contours of the transfer RNA molecules represent a specific base sequence, for each molecule (upper part) and a common terminal nucleotide sequence (lower part) to which the specific amino acids (aa_1–aa_7) are attached. Ribosomal RNA is depicted as a helix but this is only for convenience of exposition. The complementary nature of the interaction of transfer RNA and ribosomal RNA is suggested by the complementarity of their contours. (From Hoagland, M. B., Zamecnik, P. C., and Stephenson, M. C., in "Symposium on Molecular Biology," Zirkle, R. E., ed., University of Chicago Press, 1959.)

Formation of the Polypeptide Chain and its Release from the RNA Matrix

When the amino acid sequence is complete, the amino acids in some unknown manner are joined together by means of peptide bonds to form the completed polypeptide chain. Little is known concerning the way in which the final three-dimensional structure of the protein is obtained, or how the secondary bonds, particularly disulfide linkages, are formed. It has been suggested that the RNA matrix may be convoluted so that when the polypeptide chain is formed its spatial arrangement brings amino acids (particularly cysteine) close together in space, enabling them to react easily to form the secondary disulfide bond.

Still unknown is the manner in which the final assembled polypeptide chain or protein is removed from the soluble RNA molecules, or the mechanism by which the soluble RNA molecules break their hydrogen bonding to the RNA matrix.

Further Questions

Of many other questions still remaining, two of interest are "What is the basis for the specificity relationship between transfer RNA and its activating enzyme?" and "How much of transfer RNA is attached to the larger microsomal matrix RNA by means of hydrogen bonds?"

It should be pointed out that the above sequence of chemical reactions in protein synthesis applies to a particular tissue, rat liver, and for a particular portion of the cell, the microsomal and soluble fractions. There are other structures in rat liver cells, particularly the nucleus and mitochondria, that are capable of carrying out protein synthesis independently. Some aspects of protein synthesis in these structures appear to be the same as those already described but others are different, and it is possible that the mechanisms of protein synthesis vary somewhat from one structure to the next or from one species to another.

However, the fact that soluble RNA has been isolated from a simple organism like yeast, plus the observation that puromycin, which interferes with transfer RNA, stops protein synthesis in a wide variety of organisms ranging from an alga to man, argue for a basic uniformity in the mechanism of protein synthesis.

Present research is directed towards determining in more detail the relationships among DNA, RNA, and protein synthesis. Efforts are being made to isolate single species of transfer RNA so that their properties and structure can be determined.

Some success has been obtained already in this direction and within the next 25 years we may hope to see the solving of some of the many puzzling aspects of this magnificently devised process for the exact and unerring dupliciation of the extremely complex protein molecule.

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✦ ✦ ✦

Chem Ed

BOOK REVIEWS

Advanced Organic Chemistry

G. W. Wheland, University of Chicago, Chicago, Illinois. 3rd ed. John Wiley & Sons, Inc., New York, 1960. xi + 871 pp. Figs. and tables. 16 × 23.5 cm. $17.50.

With this third edition Professor Wheland maintains his reputation as the most verbal and superbly critical of the American authors of books on organic chemistry. This book contains chapters, particularly those on Stereoisomerism, Configuration of Carbon Compounds, and The Stereochemistry of Carbon, which are the most careful and sophisticated presentations of the *fundamentals* of their subjects to be found in any single volume.

The first edition of this book was not publicly offered so that the nominal second edition of 1949 was actually the first available. When one compares a *beginning* organic text of 1949 with a *beginning* text of 1960 he is struck by the almost revolutionary change in the nature of the material covered. The beginning student is now almost universally trusted with theoretical concepts and mechanisms thought too advanced for him 11 years ago and thus placed in the advanced curriculum at that time. Because of the radical nature of this shift in emphasis it is not reasonable to expect that any advanced text of 1949 could retain its function as a *text* by simple revision or editing in 1960. Wheland recognizes this fact and has chosen to alter the expected *function* of his book rather than alter its approach to any significant degree. Thus, in his Preface to the second edition of 1949 Wheland described his book as "a textbook for a course in advanced organic chemistry." However, in his Preface to this third edition the author states that it is "largely restricted to those aspects of the science that seem . . . to be inadequately treated in the other textbooks and reference books that are now available." The author also gives recognition to the fact that at his own institution, "one-half to two-thirds of the second year of organic chemistry is devoted to the material that, although omitted [from this book] can be obtained from many [other] excellent textbooks and reference books." Thus, this book is not a *text* but rather a unique reference, a reference in depth on a number of topics taken for granted in most texts of advanced organic chemistry.

Since 1949 there have been published a number of excellent advanced organic chemistry texts, all somewhat similar in reflecting a trend toward the presentation of the subject through a mechanistic approach utilizing the early introduction of theory into the elementary courses. In his new edition Wheland has not used this approach but nevertheless shows an admirable willingness to refer the reader directly to specific pages in these texts when they elaborate a point to his satisfaction. The new topics introduced into this edition, such as S_N1, S_N2, S_N2' and S_N' mechanisms, Hammett rho-sigma relations, methods of deducing reaction mechanism etc., are treated extremely briefly. However, the reader is, in each case, referred to a modern text covering the subject adequately.

The order of the chapters in the first part of the new edition has been altered extensively and effectively. The cuts of structural formulas are all new and considerably improved over the earlier edition. Wheland's reluctance to succumb to the now generally accepted mechanistic symbolization using the curved arrow to represent an electron shift will make his occasional reference to mechanism rather difficult for the student to follow.

Updating the textual material has been done in two ways. A portion of the exposition has been left essentially unchanged from the previous edition but references to more modern literature dealing with each subject have been added in context. In other portions of the book the material has been rewritten. Of the over 1100 references (many multiple) almost half include direction to papers or books appearing since the second edition of the book was published.

It is unfortunate that the cost of the book (more than double that of the earlier edition) will preclude much individual ownership, for it is with leisurely examination that the finer points of Wheland's arguments are fully appreciated.

QUENTIN R. PETERSEN
Wabash College
Crawfordsville, Indiana

Experimental Biochemistry

Gerald Litwack, University of Pennsylvania, Philadelphia. John Wiley & Sons, Inc., New York, 1960. xv + 313 pp. Figs. and tables. 15 × 23 cm. $5.50.

This is a good book for undergraduate and beginning graduate students well prepared in organic chemistry. Most of the experiments can be done with equipment usually available in a biochemistry laboratory, such as an electronic photometer. Four sections deal with carbohydrates, lipids, amino acids and proteins, and enzymes. The enzyme section is the largest.

Many new experiments stress modern quantitative instruments and use of microorganisms. They introduce elementary enzyme kinetics, with use of Thunberg tubes, Barcroft-Warburg manometry, and the Conway microdiffusion technique. There is an experiment on the enzymic decarboxylation of glutamic acid labelled with radioactive carbon. These are a few examples.

This is not just another biochemistry cookbook with the traditional isolation of cystine from hair, etc. It is full of exciting new experiments with the look of modern research. By working in pairs or groups and having more than one experiment on stream at a time, the students have a chance to get to know what a research team is like. And they know what is going on, thanks to the extensive theoretical discussion preceding each experiment. Use of this manual in the student laboratory should be refreshing to the instructor and stimulating to the student. Everyone concerned with the teaching of biochemistry should examine a copy for himself.

A. R. PATTON
Colorado State University
Fort Collins

Reviewed in this Issue

G. W. Wheland, Advanced Organic Chemistry

Gerald Litwack, Experimental Biochemistry

Arnold Weissberger, Editor, Physical Methods of Organic Chemistry. Part 2

Stanislas Dockx, Theorie Fondamentale du System Periodique des Elements

Edward Cartmell, Chemistry for Engineers The Harvey Lectures. Series 54

The Harvey Lectures, Series 54

R. C. Vickery. The Chemistry of Yttrium and Scandium

A. A. Smales and *L. R. Wagner*, Editors, Methods in Geochemistry

M. Stacey, J. C. Tatlow, and *A. G. Sharpe*, Editors, Advances in Fluorine Chemistry. Volume 1

P. A. Ongley, Tutorial Questions in Organic Chemistry

Lawrence J. Heidt, Robert S. Livingston, Eugene Rabinowitch, and *Farrington Daniels*, Editors, Photochemistry in the Liquid and Solid States

Jerome S. Bruner, The Process of Education

M. Frank Mallette, Paul M. Althouse, and *Carl O. Clagett*, Biochemistry of Plants and Animals

H. K. King, The Chemistry of Lipids in Health and Disease

H. Teuscher, R. Adler, and *Jerome P. Seaton*, The Soil and Its Fertility

Physical Methods of Organic Chemistry. Part 2

Edited by *Arnold Weissberger*, Research Laboratories, Eastman Kodak Co., Rochester, New York. 3rd revised ed. Interscience Publishers, Inc., New York, 1959. xii + 935 pp. Figs. and tables. 16 × 23.5 cm. $24.50.

This volume continues the high level which we expect of the series. The Table of Contents is: XVI. Determination of Diffusivity, by A. L. Geddes and R. B. Pontius*; XVII. Determinations by the Ultracentrifuge, by J. Burton Nichols and the late Emerson D. Bailey; XVIII. Refractometry, by N. Bauer*, K. Fajans, and S. Z. Lewin; XIX. Determination of Crystal Morphology, by the late M. A. Peacock, J. D. H. Donnay*, and Gabrielle Donnay*; XX. Crystallochemical Analysis, by J. D. H. Donnay* and Gabrielle Donnay*; XXI. Light Microscopy by Edwin E. Jelley; XXII. Microspectroscopy, by Elkan R. Blout; (N)XXIII. X-Ray Microscopy, by W. C. Nixon; XXIV. Electron Microscopy, by F. A. Hamm; XXV. X-Ray Crystallography, by William N. Lipscomb*; XXVI. Electron Diffraction by Gases, by L. O. Brockway; XXVII. Neutron Diffraction, by J. M. Hastings and L. M. Corliss.

Chapter XXIII on X-Ray Microscopy is new as indicated by the (N) in the Table of Contents above. Each of those whose name is followed by an asterisk is also a new author in this edition compared to the previous edition. It will be seen that the major part of this volume does not involve new authors or completely new material.

It seems safe to say that there is no other source book which as compactly and as authoritatively as this one presents the latest information in the fields which it covers.

J. A. Campbell
Harvey Mudd College
Claremont, California

Theorie Fondamentale du System Periodique des Elements

Stanislas Dockx, L'Institute International des Sciences Theoriques. Office International de Librairie, Brussels, Belgium, 1959. 183 pp. 29 tables 16 × 25 cm. Paperbound. $6.06.

This book is not recommended. The fundamental theory turns out to be a fantasy based on an avoidance of facts and a misapprehension of wave mechanics.

Dockx begins by rearranging the periodic system to get a more symmetrical structure from which the regular mathematical basis underlying the system can be abstracted. His new table is a IIIC3-4 type (Mazur's classification). In this process certain theorems are derived which give the order in which the various subshells must be filled. When irregularities occur in the order of filling (as at Cr, Cu, La, and Gd, for example) the accepted ground states are said to be "experimentally arbitrary and theoretically inexact" and the irregularities are eliminated.

As a fair example of Dockx's methods consider page 76. Here it is said that, "... only Gd, La, and Lu from among the rare earths have, for theoretical rather than experimental reasons, a 5*d* electron in their basic structure." Dockx goes on to say that this change from Bohr's early predictions is not surprising because, as Yost says (Yost, Russell, and Garner, "The Rare-Earth Elements and their Compounds," pp. 2-3, Wiley, New York 1949), "the complexity of the rare earth spectra is so great that no definite prediction can be made in the absence of a fundamental theory." Now the exact quotation from Yost, Russell, and Garner is given in an English footnote and goes, "... that no definite prediction, based on a fundamental theory, can be made." Moreover, on the same page of Yost, Russell, and Garner is the statement that "The ground states of seven of the rare earths in the neutral state ... have been established with considerable certainty" and among these seven are La and Gd with 5*d* electrons. The certainty is not considerable enough to prevent the statement on p. 78 that, "These modifications in the electronic structures of La and Gd [the elimination of the 5*d* electrons] which we propose here are not in opposition to the experimental data."

More examples could be cited but it would all come to the same thing in the end—this book is not recommended.

Russell F. Trimble, Jr.
Southern Illinois University
Carbondale, Illinois

Chemistry for Engineers

Edward Cartmell, University of Southampton, England. Butterworth and Co. (Canada) Ltd., Toronto, 1959. vii + 172 pp. Figs. and tables. 14.5 × 22 cm. $5.

Brevity is the word which describes this book "Chemistry for Engineers" by Edward Cartmell. As the author explains it is designed primarily to serve as an introduction of chemistry to engineers who in their course of training will not take chemistry. This is direct contrast to the average curriculum in the United States where a thorough one year course in chemistry is the minimum requirement.

The text presentation emphasizes nuclear chemistry, atoms and molecules, chemical fuels, metals, corrosion and water treatment. In no case is the development in detail but the material is presented so that it may be understood without a chemical background. The inclusion of the section on atoms and molecules previous to that on nuclear chemistry would help the reader.

This book is not recommended except as an introduction to chemistry for engineers and as an example of what the British consider important to the engineer. It should not be used as a text for students in chemistry or engineering.

George M. Machwart
Michigan College of Mining and Technology
Houghton, Michigan

The Harvey Lectures. Series 54

Delivered under the auspices of the Harvey Society of New York, 1958–1959. Academic Press, Inc., New York, 1960. vi + 312 pp. Figs. and tables. 14 × 21 cm. $7.50.

The Harvey Society, organized during the spring of 1905, sponsored its first public lecture at the New York Academy of Medicine on October 7, 1905, and presented its first bound set of lectures to the public in 1906. It was of interest to the reviewer of this particular number in this famed series of publications to explore the goals of the society as stated at its inception to see whether or not the lectures of the present era still measured up to early norms. I have picked statements at random as they appear in the first collection of The Harvey Lectures (1905–1906) to set forth the newly founded society's goals: —"Its avowed object is the diffusion of the medical sciences by means of public lectures.—The lectures are not intended to be merely accounts of experimental work done by the lecturers. They are rather to be a broad presentation—(which) includes a resume of the experimental work done on the subject, and a critical review of this work in the light of the most recent advances." As organized and initiated by Professor Graham Lusk, the society's first president, these were the hopes to be attained.

More than half a century has passed since then and this reviewer, for one, must enthusiastically compliment the Harvey Society for so gallantly achieving its stated purpose. The present collection of nine lectures is no exception; distinguished investigators in their respective fields have again compiled pertinent experimental data and critically surveyed the general subject.

The lectures included in this number of the series are Genetic Control of Viral Functions by Francois Jacob, Metamorphosis and Body Form by V. B. Wigglesworth, Methods of Approach to the Problems of Behavior by K. Lorenz, The Excretory Function of the Liver by S. E. Bradley, and Excitation and Inhibition in Single Nerve Cells by S. W. Kuffler. The other four lectures are more specifically in the biochemical area, including The Enzymatic Synthesis of the Purine Nucleotides by J. M. Buchanan, Metabolic Studies with Normal and Malignant Human Cells in Culture by H. Eagle, Carotenoid Pigments: Problems of Synthesis and Function by R. Stanier, and finally Historic and Current Aspects of the Problem of Protein Synthesis by P. C. Zamecnik.

This, as usual, is another compact volume convenient to carry most anywhere. It is pleasant yet stimulating reading. For the investigator and teacher, it is educational in less familiar fields and integrating in areas of personal interest. For the student, it is a most valuable source for supplemental reading. This book is heartily recommended to all.

Eugene E. Dekker
The University of Michigan
Ann Arbor, Michigan

(*Continued on page A268*)

COLLEGE CHEMISTRY. A Systematic Approach. *Second Edition*

By HARRY H. SISLER, University of Florida, and CALVIN A. VANDER WERF and ARTHUR W. DAVIDSON, both of the University of Kansas

1961, 709 pages, Ill., $7.50

In this up-to-date edition, the authors examine the major theoretical principles of the structure of matter and chemical reactions, emphasizing the correlation of structure and properties of substances in our physical environment. New chapters on nuclear chemistry and rocket fuels are included, and there are numerous exercises and illustrations.

TEXTBOOK OF INORGANIC CHEMISTRY

By S. YOUNG TYREE, University of North Carolina, and KERRO KNOX, Bell Telephone Laboratories

1961, 434 pages, Ill., $7.00

This textbook, designed for introductory courses in inorganic chemistry, provides students lacking background in physical chemistry with a clear understanding of basic chemical behavior and the latest theoretical concepts. For each group of elements the authors describe occurrence, history, preparation, physical properties, chemical properties, and the uses of compounds.

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By SAMUEL H. MARON, Case Institute of Technology, and CARL F. PRUTTON, Food Machinery and Chemical Corporation

1958, 789 pages, Ill., $8.50

This edition offers compact presentation of the material; information on recent developments in physical chemistry; 634 problems; and rigorous mathematical treatment, particularly in the discussions of thermodynamics and chemical equilibrium.

Answer to problems available gratis

QUANTITATIVE CHEMICAL ANALYSIS, *Eleventh Edition*

By LEICESTER F. HAMILTON and STEPHEN G. SIMPSON, both of the Massachusetts Institute of Technology

1958, 566 pages, Ill., $6.25

Here is an introductory text which provides an effective balance between theoretical discussions and laboratory procedures, stoichiometric principles and practical suggestions. It includes material on such modern topics as coulometric methods, numerical problems in optical methods, and the bromate and iodate processes.

INSTRUMENTAL ANALYSIS

By PAUL DELAHAY, Louisiana State University

1957, 384 pages, Ill., $8.25

Focusing on the fundamentals of instrumental analysis, this text covers three main methods groups: electrochemical; spectroscopic; and such miscellaneous techniques as X-rays, mass spectrometry, and radioactivity. More than fifty experiments, numerous graded problems, and a detailed bibliography are included.

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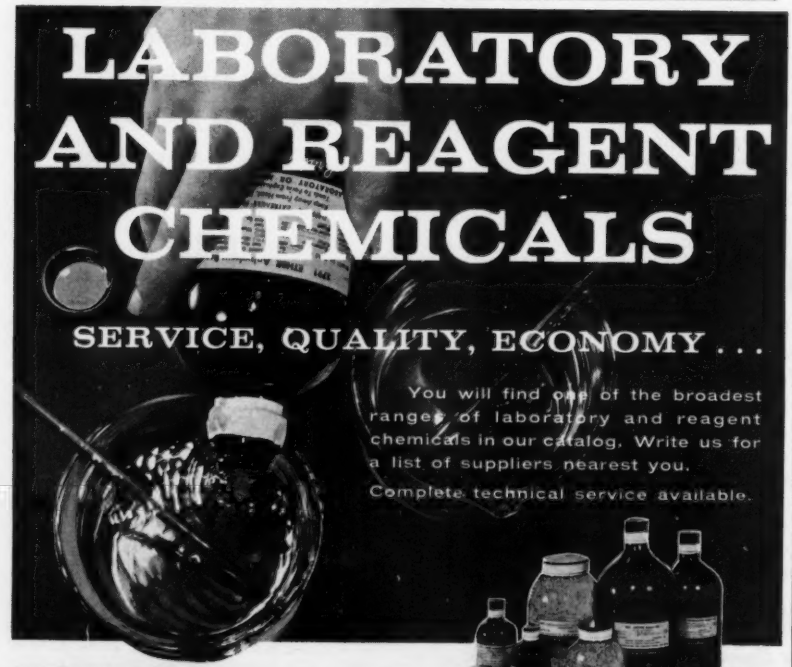

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BOOK REVIEWS

The Chemistry of Yttrium and Scandium

R. C. Vickery. Pergamon Press, Inc., New York, 1960. vii + 123 pp. Figs. and tables. 16 × 23 cm. $6.50.

This small volume is a logical extension of and supplement to the author's more comprehensive "Chemistry of the Lanthanons" and is remarkably like its predecessor in approach, style, and coverage of subject matter. Much of what was said relative to the earlier volume (J. CHEM. EDUCATION, *31*, 443(1954)) is, therefore, completely applicable to this one.

The author treats in some detail the historical and mineralogical background of these two elements and then covers their separation and purification and the properties of the metals and their compounds. The treatment is essentially descriptive, with only minor emphasis upon any theoretical or semi-theoretical concepts. Although the coverage of the descriptive chemistry of the two elements is extensive, it is by no means encyclopedic, and many aspects are handled more by references to the original literature than by actual discussion. This is particularly true, for example, of separations by the ion-exchange method and of the characteristics of many types of compounds. A full appreciation of the chemistry of yttrium and scandium requires that the "Chemistry of the Lanthanons" be consulted in conjunction with the present volume.

Unfortunately, the author must again be criticized to some extent for his carelessness in handling material from the literature, although such errors in this book are far less frequent than those in its companion volume. For example, no distinction is made between H. C. Kremers and H. E. Kremers, both of whom have contributed extensively to these fields, and the Pokras dissertation (page 97) was not submitted at the University of Illinois. Furthermore, to pick isolated items at random, anhydrous nitrates are not obtainable by electrolysis (page 59), and the nomadic position of ytrrium in separations cannot be associated with the stability of its complexes (page 51). Unfortunate items of this type detract somewhat from the good points that the book has in bringing together the widely scattered information on these interesting and useful elements.

The book is entirely a reference and as such will be of primary interest to libraries and to workers dealing only with these and related elements. Interest in the book would be broadened if it were more moderately priced.

THERALD MOELLER
University of Illinois
Urbana, Illinois

(*Continued on page A270*)

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BOOK REVIEWS

Methods in Geochemistry

Edited by *A. A. Smales*, Atomic Energy Research Establishment, Harwell, England, and *L. R. Wagner*, University Museum, Oxford University. Interscience Publishers, Inc., New York, 1960. vii + 464 pp. Figs. and tables. 16 × 23.5 cm. $13.50.

This book deals with instrumental methods of analysis and would be a more interesting text for a course in Instrumental Analysis than many textbooks designed for such courses. Thirteen British authorities contribute 11 chapters covering flame photometry, colorimetry, spectroscopy, X-ray fluorescent spectrography, mass spectrometry, radiochemistry, neutron activation analysis, polarography, and ion exchange methods.

The material is covered with thoroughness in explicit detail, as for example the paragraph on page 35 entitled Precision (Reproducibility) and Accuracy (Approach to the Truth). Many references to the original literature are given, e.g., 167 references at the end of chapter 7. Not all of these references are correctly correlated with the text, as for example the reference on page 52 to reference 20 at the end of chapter 3.

Reference is made to instruments which are largely of British manufacture, e.g., the Evans Electroselenium, Ltd., flame photometer, which may limit the usefulness of the book slightly in the U.S. However, to those teachers who try to impart the theory of the method to their students it will make little difference whether the "black box" in the illustration is a Univector polarograph (Fig. 7, opposite page 376) or the Sargent Model XII.

Some excellent illustrative material is provided such as the flow sheet for rapid silicate analysis from the U. S. G. S. Bulletin 1036-C on page 73, and the chart of half wave potentials for polarography on page 364 which is more extensive than that of V. Majer, *Chem Rev.*, **24**, 74 (1939).

Some of the material, such as chapter 4 by Taylor and Ahrens which covers spectrochemical analysis in 26 pages, may seem a little brief. Closer examination shows, however, that most of the important points are covered and adequate references to other sources for more details are given. Such an approach is about right for a geologist who wants to do some spectroscopy but does not want to wade through all the detail in one of the longer treatises on spectroscopy.

Two chapters are devoted to the mass spectrometer, one of the most useful tools to the geochemist. One chapter deals entirely with isotope dilution analysis with which cesium in gold foil can be detected with a sensitivity of 10^{-6} microgram. The chapter on neutron activation analysis by D. Mapper of the Harwell Laboratory includes references up through 1958, such as the interesting work of Smales, Mapper, and Wood on the analysis of micrometeoritic spherules by this method.

The sometimes baffling (to U. S. readers) British tradition of indexing is maintained. For example, the reader will have to find "step sector" on page 98 for himself, but "jaw-breakers, laboratory" are carefully located for him on page 13 as the only entry under J.

J. A. Schufle
New Mexico Institute of Mining and Technology
Socorro

Advances in Fluorine Chemistry. Volume 1

Edited by *M. Stacey* and *J. C. Tatlow*, both of University of Birmingham, England, and *A. G. Sharpe*, Cambridge University, England. Academic Press, Inc., New York, 1960. vii + 203 pp. Figs. and tables. 16 × 25 cm. $8.

A few years ago several highly authoritative review articles appeared in "Fluorine Chemistry," volumes 1 and 2, edited by J. H. Simons. The valuable and useful service of this sort of publication is now being continued in "Advances in Fluorine Chemistry." The editors "hope to make the series international and to attract articles from leading investigators in every country." They "intend to report in turn on fundamental advances in all major branches of the subject and to provide accounts of developments in the industrial field."

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(*Continued on page A272*)

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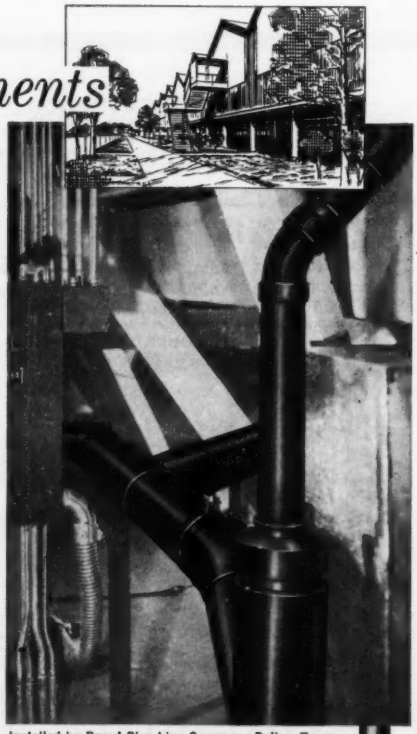

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References

(1) Ind. Eng. Chem. 26-653 (June, 1933)

(2) Ind. Eng. Chem. 25-1112 (Oct., 1933)

(3) National Bureau of Standards Journal of Research 12-241 (Feb. 1934, R.P. No. 649)

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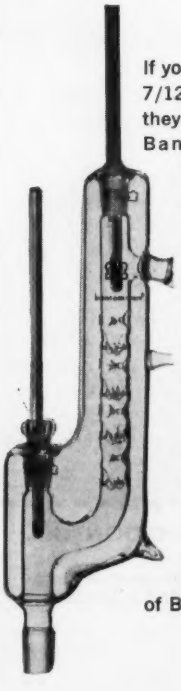

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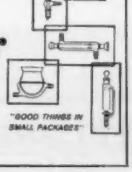


BOOK REVIEWS

ference on Fluorine Chemistry held in Birmingham University, England, in the summer of 1959. These are thoroughly documented and bring the reader up to date (into 1958). They are of greatest value to those engaged in research in the fields covered but may be easily understood by all chemists. The topics covered are: (1) The Halogen Fluorides–Their Preparation and Uses in Organic Chemistry by W. K. R. Musgrave, University of Durham, England; (2) Transition Metal Fluorides and Their Complexes by A. G. Sharpe, Cambridge University, England; (3) Fluoboric Acids and Their Derivatives by D. W. A. Sharp, Imperial College, London; (4) The Electrochemical Process for the Synthesis of Fluoro-organic Compounds by J. Burdon and J. C. Tatlow, University of Birmingham, England, (5) Exhaustive Fluorinations of Organic Compounds with High-Valency Metallic Fluorides by M. Stacy and J. C. Tatlow.

Even though these reviews are very thorough, it is still possible to detect the nature of the interest of the authors in the topics. For example, topics 1, 4, and 5 are obviously written by men interested in the synthesis of organic compounds while topics 2 and 3 are written by inorganic chemists. The part of the book which is most likely to be of general interest to teachers of chemistry is the fine discussion by A. G. Sharpe on pages 29 to 35 of the reasons why some fluorides are ionic while others are covalent. This part of the book goes beyond the bounds of a review. Organic chemists, in general, should be interested in the numerous fluoro-cyclohexanes described by Stacey and Tatlow on pages 176 to 181.

Volume 1 of this series is a fine beginning. Surely all "fluorine chemists" will await future volumes with much interest.

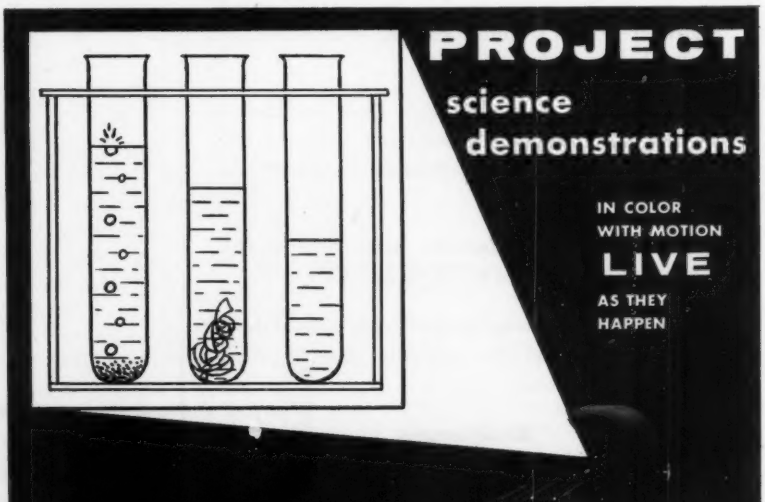
GEORGE H. CADY
University of Washington
Seattle Washington

Tutorial Questions in Organic Chemistry

P. A. Ongley, College of Technology, Birmingham, England. University of London Press Ltd., London, 1959. xii + 276 pp. 14.5 × 22 cm. 21/-.

The author of this book has compiled a series of questions and problems, partly selected from the examinations of 22 universities in the United Kingdom, to aid a student in the application and coordination of his knowledge of organic chemistry. These questions, found in the first division of the book, are grouped specifically for the various classes of organic compounds. Each group is further subdivided into two sets. Set A contains more elementary concepts and could be answered by students having had a basic course in organic chemistry. Set B is for a more advanced group. In each set the questions are given in progressive difficulty and apparently follow a

(*Continued on page A276*)



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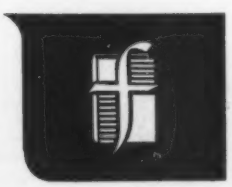

definite pattern; namely, nomenclature, completion reactions, preparations, distinctions, separations, and problems. Since no descriptive material is given, a student needs a previous understanding of how to approach these types of problems.

The answers for all questions and problems, given in the second section, are brief and in some instances might leave a weak student uncertain. For example, the type of process, such as oxidation, is given but the actual reagent and conditions are not mentioned.

A third section of the book contains a summary of the rules of nomenclature, a list of trivial names with formulas, and a list of common named reactions with their conditions and variations. The nomenclature rules follow those set forth by the *Journal of the Chemical Society* and Geneva convention (no reference is made to I.U.C. or I.U.P.A.C.), and differ slightly from those in *Chemical Abstracts*.

Although this book is primarily a guide to the types of questions and problems to be expected on examinations in the British universities, it has merit in that it emphasizes the fundamentals and interrelationships of organic chemistry. It should be noted no questions appear on the more recent theoretical concepts now being introduced into beginning organic chemistry.

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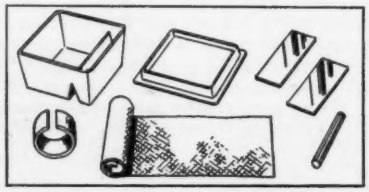

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Photochemistry in the Liquid and Solid States

Edited by *Lawrence J. Heidt*, Massachusetts Institute of Technology, Cambridge, *Robert S. Livingston*, University of Minnesota, Minneapolis, *Eugene Rabinowitch*, University of Illinois, Urbana, and *Farrington Daniels*, University of Wisconsin, Madison. John Wiley & Sons, Inc., New York, 1960. vi + 174 pp. Figs. and tables. 22 × 28.5 cm. $6.

This is a collection of papers presented at a symposium held at Dedham, Massachusetts, September, 1957, which had been arranged by a subcommittee of the National Research Council and the National Academy of Sciences on the photochemical storage of energy. Most of the papers were published in the *Journal of Physical Chemistry*. It is unfortunate that the editors did not include the discussions of the papers made at the meeting. The reviewer had the good fortune to be present and recalls that the discussions were often as interesting as the papers themselves and usually dealt with more fundamental questions in photochemistry than did the papers.

The editors have summarized the criteria for photochemical reactions which would utilize solar radiation. None of these systems discussed at the meeting, photosynthesis excluded, even approximate the properties desired. The silicon cell is an excellent solar energy converter but it has no electrical storage capacity. Efficient photochemical systems yet to be found could avoid this difficulty.

It is not feasible to review all the 25 excellent papers which are reprinted in the book. A few general remarks are in order, however. No explanation of the purely photochemical aspects of photosynthesis has been presented. No explanation of the nature of the latent image in silver halide photography has been presented. Thus, despite the efforts of photochemists, the biggest questions remain unanswered.

GERALD OSTER,
Polytechnic Institute of Brooklyn,
Brooklyn, New York

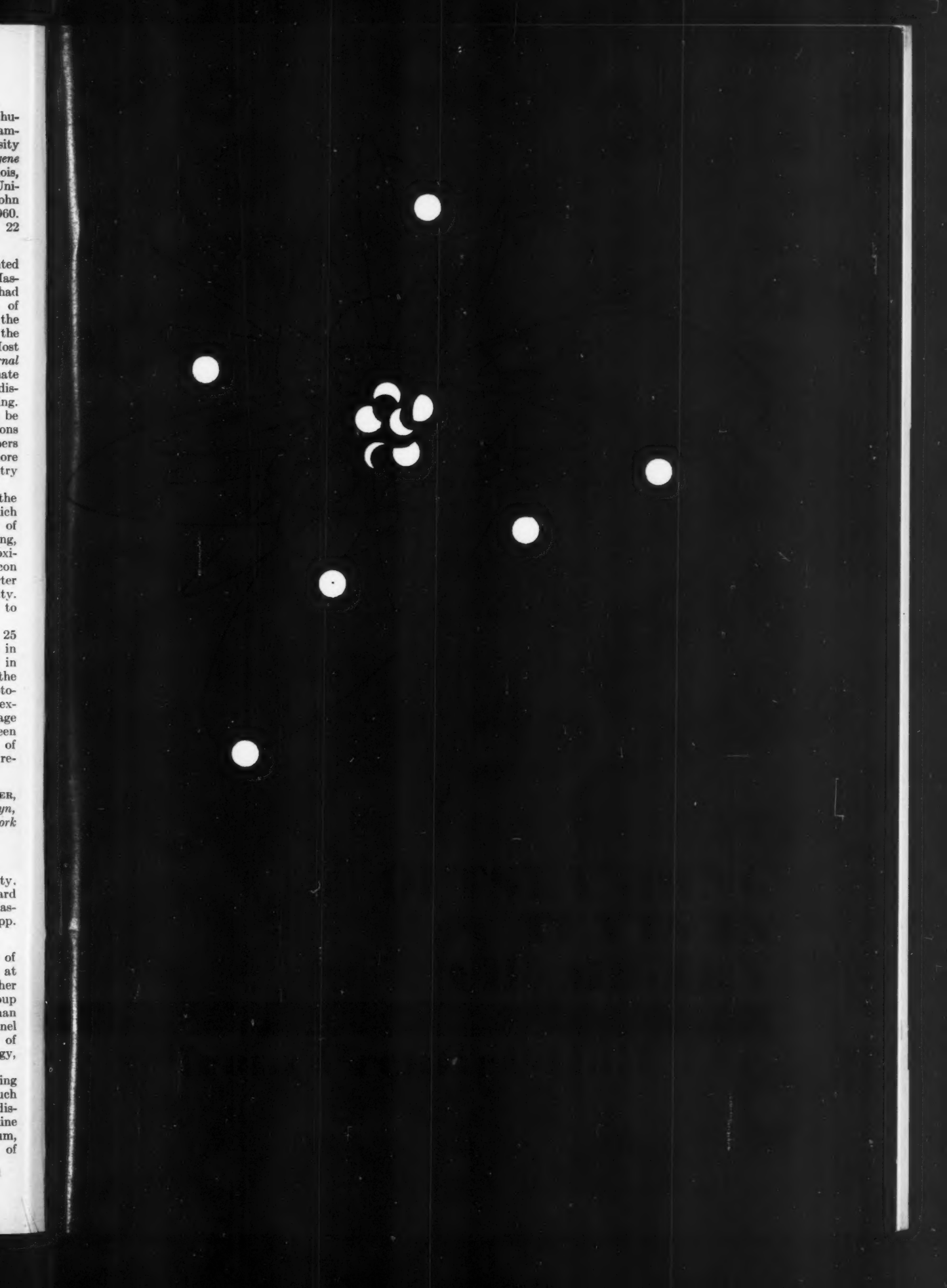
The Process of Education

Jerome S. Bruner, Harvard University. Cambridge, Massachusetts. Harvard University Press, Cambridge, Massachusetts, 1960. xviii + 97 pp. 14 × 20.5 cm. $2.75.

This book makes public the "sense of the meeting" from a conference held at Woods Hole in 1959. It differs from other reports, as the title suggests. This group was less concerned with content than with process of education. The personnel consisted of 34 men from the fields of science, history, language, psychology, and education.

After preliminary sessions for reviewing reports of subject-matter studies (such as the PSSC), the members were distributed into five work groups to examine these topics: Sequence of Curriculum, Apparatus of Teaching, Motivation of

(*Continued on page A282*)



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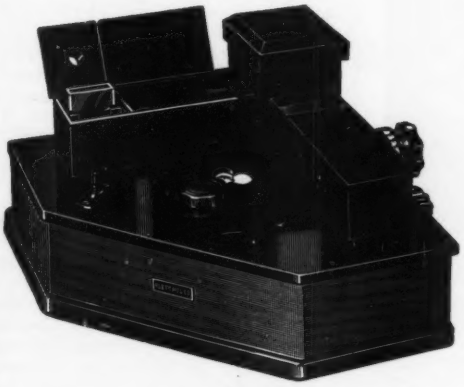

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Learning, Role of Intuition in Learning, and Thinking and Cognitive Processes in Learning. Each group prepared its report upon its particular topic. The author summarizes these and the review of each by the conference as a whole.

He does more, however, than merely summarize and report. He attacks the problems of education astutely and directly. It is refreshing to find such new education perspectives emphasized in such good writing. The author states: "A basic assumption throughout the discussions was that the foundations of any subject may be taught to anybody at any age in some form," and that "intellectual activity anywhere is the same whether at the frontier of knowledge or in a third grade classroom."

Some tentative proposals that emerged from the conference were: Learning that is both understood and retained must have relevance to the structural form of the subject; if one respects the way of thought of the growing child, it is possible to introduce him, at an early age, to ideas and styles that, in later life, make an educated man; there is warrant to be concerned over failure to distinguish between articulate idiocy and inarticulate genius. Understandings are possible to those who may not be able to formulate them; the late bloomer, the early rebel, the child from the educationally indifferent home must not become the victims of ossified "meritocracy"; we cannot afford to alienate the "literary intellectuals" who may consider preferential awards for scientific achievements as an abandonment of traditional culture. In other words, improved curricula for the humanities and the social sciences warrant public concern as well as current attention to the natural sciences and mathematics.

Need it be said that this attention to the learning process should receive considered emphasis comparable to that given the content studies of subject matter? For after all, education involves *students* as well as teachers and course content. While it is generally conceded that one cannot teach something he does not know, the Woods Hole group would add that the "known" should include the "to whom" as well as "the what."

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Biochemistry of Plants and Animals

M. Frank Mallette, Paul M. Althouse, and *Carl O. Clagett,* all of Pennsylvania State University, University Park. John Wiley and Sons, Inc., New York, 1960. xii + 552 pp. Figs. and tables. 15.5 × 23.5 cm. $8.50.

This book gives a broad treatment of agricultural biochemistry at an elementary level. It originated from and was designed to replace "Introduction to Agricultural Biochemistry" by Dutcher, Jensen, and Althouse (Wiley, 1951). Very few changes were made in types of subject covered in this text; however, most of the chapters were completely rewritten and brought up to date. Less emphasis was placed on the historical development of biochemistry and more emphasis was placed on recent advances than in the original text.

The book is divided into three parts entitled General Biochemistry, Plant Biochemistry, and Animal Biochemistry. The first part includes a brief history of the development of agricultural biochemistry, a chapter on the properties of matter which reviews elementary physical chemistry related to biochemistry, chapters on the main classes of biochemical compounds and a chapter on energy transfer and biological oxidation.

Part 2 on plant biochemistry includes an elementary discussion of plant structure and composition followed by a completely revised chapter on plant metabolism which covers the basic metabolic reaction involved in photosynthesis and the metabolism of carbohydrates, lipids, and nitrogen compounds. The detailed discussion of seed germination contained in the previous book is reproduced in chapter 10 of this book. The chapters on soils and fertilizers found in the parent book were condensed and included in the chapter on plant nutrition along with the discussion of the essential mineral elements. A new chapter, entitled Growth Regulation, contains a discussion of the environmental factors influencing growth and a discussion of plant hormones and regulators. This section, like most of the other sections in the book, will acquaint students with the fundamental principles of the subject but does not go into the subject in great detail.

(*Continued on page A284*)

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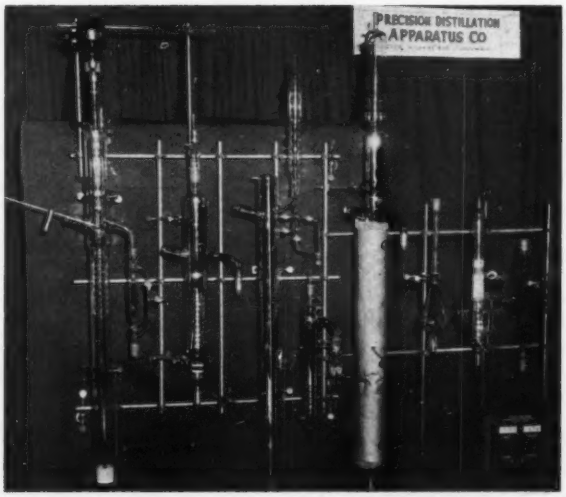

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BOOK REVIEWS

Part 3 on animal biochemistry covers this area rather thoroughly and includes some chapters on subjects which are not commonly discussed in detail in elementary biochemistry texts. The composition and function of various body tissues are discussed in sufficient detail to give students a basic understanding of animal physiology. The chemistry, function, requirements, and deficiency symptoms of vitamins are covered adequately in chapter 14. Chapters on the metabolism of minerals, carbohydrates, lipids, and proteins were completely revised and brought up to date. The composition of feeds from various sources is presented in chapter 16 in much the same way as in the previous text; however, sections on antibiotics and hormones were added in the current text. A general discussion of the energy content of food is given in the last chapter.

An appendix consisting of 12 tables tabulates the recent data on food and feed composition and nutritional requirements of human beings and farm animals.

Although this book is oriented toward students in the agricultural sciences the coverage is broad enough that the book could be used as an elementary text in biochemistry in other disciplines.

H. E. PARKER
Purdue University
Lafayette, Indiana

The Chemistry of Lipids in Health and Disease

H. K. King, University of Liverpool, England. Charles C Thomas, Publisher, Springfield, Illinois, 1960. viii + 104 pp. Figs. 15.5 × 23.5 cm. $3.75.

Perhaps the most important problem in clinical medicine today is the biochemistry of the condition known as atherosclerosis in which the metabolism of the lipids is alleged to play an important role. As stated in the preface of this book "A problem faces the medical man whether he be a student, in practice, or engaged in research who wishes to understand this new situation. Excellent specialist monographs are available on most aspects of lipid biochemistry, but he will probably lack both the basic knowledge and the time to study them. I have written this book to help such people."

Actually, this is an extremely well-written discussion of the chemistry and biochemistry of the lipids with special emphasis in the last two chapters on "Lipids and Diet" and "Lipids and Atherosclerosis." Further as stated in the last chapter "It is not the purpose of this book either to put forward new theories or to sit in judgment on existing conflict. We aim rather at acquainting the reader with the factual theoretical background needed to enable him to define the problem, to understand the various protagonists, and to bring his

(*Continued on page A286*)

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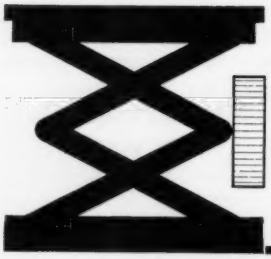

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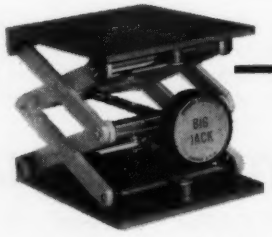

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BOOK REVIEWS

own informed judgment to bear on the opinions put forward."

Other chapters are entitled Lipids and Water, Chemical Structure of Lipids, Digestion and Absorption of Fats, Absorption and Metabolism of Sterols, Oxidative Breakdown of Fats, and Biosynthesis of Lipids. It seemed to this reviewer that the book is extremely well written and informative, and that many chemists and biochemists will enjoy reading it. Of unusual interest is Chapter 1, Lipids and Water, which is brief and informative.

J. B. Brown
The Ohio State University
Columbus

The Soil and Its Fertility

H. Teuscher, Montreal Botanical Garden, Montreal, Canada, and *R. Adler*, deceased, with the collaboration of *Jerome P. Seaton*, Purdue University, Lafayette, Indiana. Reinhold Publishing Corp., New York, 1960. vii + 446 pp. Figs. and tables. 16 × 23.5 cm. $12.

For the amateur agriculturalist, this book provides some interesting reading. The general lack of references makes the book of limited value for the trained agriculturalist. The reviewer would disagree with some of the proposals and explanations made by the authors. In their attempt to provide a complete picture of the soil and its fertility, the authors have only lightly treated many aspects. This leaves the reader with a feeling that the soil is a complex substance, and that our knowledge of it is only a collection of miscellaneous facts.

The book seems to be disjointed—difficult at times to follow from one topic to another. In many instances, various topics are discussed under headings which bearly hint of association. The authors dwell upon the organic fraction of the soil and its importance in crop production. The emphasis seems unfounded due to the lack of sufficient supporting scientific data.

The section entitled The Laws of Soil Fertility seems out of place in a book of this kind, since the authors go into considerable detail. The discussion of fertilizers and their use is quite limited and examples given in many instances are not typical. One of the most important aspects of crop production, water, is only lightly touched. By comparison to other books on the same subject this book fails to improve upon that which is already in print.

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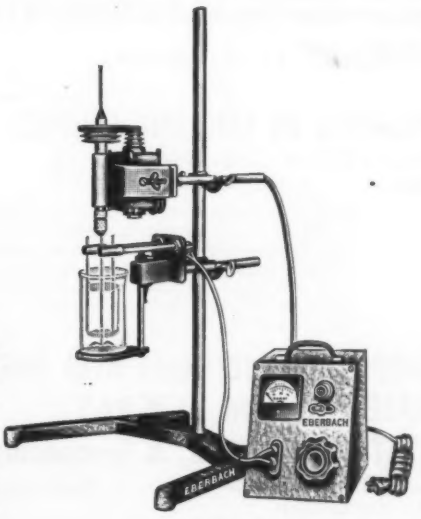

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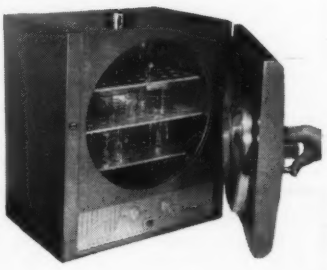

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DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5 X 8 CARDS

Photochemical Catalysis of an Aliphatic Substitution Reaction

A Chem Ed TESTED DEMONSTRATION

Submitted by: Harold Hart, Michigan State University, East Lansing
Checked by: D. A. Driesbach, Hiram College, Hiram, Ohio

DETACH PAGE BY CUTTING ALONG THIS LINE—INDIVIDUAL DEMONSTRATIONS MAY BE CUT APART AND PASTED ON 5 X 8 CARDS

PREPARATION

Wrap an 8-in. test tube completely with friction tape, being certain that there are no gaps for light to leak in. Mount two 8-in. test tubes, one clear and one wrapped, side by side on a ring stand. Above each, mount a small (30 ml) long-stemmed addition funnel. On a separate ring stand, mount an ordinary sun lamp (Westinghouse Type RS, 275 watt), so that the middle of the lamp is at a level about one inch above the bottom of the test tubes.

Prepare a 5% (by volume) solution of Br_2 in CCl_4. Moist blue litmus and/or a bottle of concentrated ammonia should be available.

DEMONSTRATION

Place 25 ml of hexane in each test tube, and in each additional funnel place 5 ml of Br_2 solution. Bring the sun lamp within 1–4 inches of the tube, turn the lamp on, and add Br_2 rapidly by drops (total time 2–3 min) simultaneously to each of the hexane solutions. The red color will disappear as rapidly as the Br_2 is added to the unwrapped tube.

Evolution of HBr can be demonstrated by breathing out across the mouth of the tube, by the moist blue litmus, and by bringing NH_3 near.

After each addition is complete, pour the contents of the wrapped tube into a clear vessel; the solution will be deep red-brown, and will not show HBr evolution by the above tests.

REMARKS

The sun lamp should not be too close to the hexane solutions, or the latter will get hot; but ultraviolet radiation is dissipated rapidly with distance and is absorbed by the Pyrex glass. It is therefore necessary to strike a balance (1–4 inches) in positioning the lamp.

A Demonstration Answer to a Stereochemical Puzzler

A Chem Ed TESTED DEMONSTRATION

Submitted by: Harold Hart, Michigan State University, East Lansing, Michigan. The assistance of Mr. Roger Wheaton, who drew the figure, is appreciated.

PREPARATION

A drop of oil is placed on the threads of a clamp holder (see figure; CENCO 12264 or one of similar design will do) to ensure that the thumb screws turn freely. The ends of the clamp holder or the heads of the thumb screws may be painted different colors for identification. One thumb screw should be turned all the way in; the other extended nearly all the way out.

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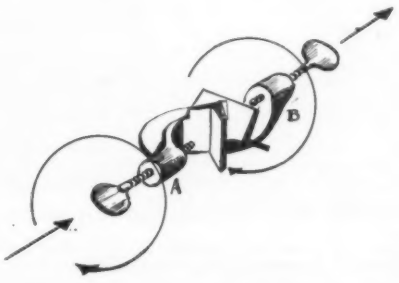
Students sometimes ask, when studying a molecule with an asymmetric carbon atom, why the different orientations of the molecule in solution do not result in cancelling the rotation of plane-polarized light. Why does not molecule *B*, located further down the polarimeter tube and oriented 180° to molecule *A*, reverse any rotation induced by *A*? This demonstration is designed to provide an answer using a mechanical analogy.

DEMONSTRATION

The student is shown a clamp holder, the ends of which consist of right-handed threads oriented at



180° to one another (corresponding to two asymmetric molecules A and B, similarly oriented). The thumb screws correspond to plane-polarized light which must pass through the molecules (from one end of the clamp holder to the other; see arrows in the figure). It is obvious from the figure that in order to pass through molecules A and B *the thumb screws must be turned clockwise for both molecules.* Therefore, despite the different molecular orientations, the light (thumb screws) will be rotated in the same direction.

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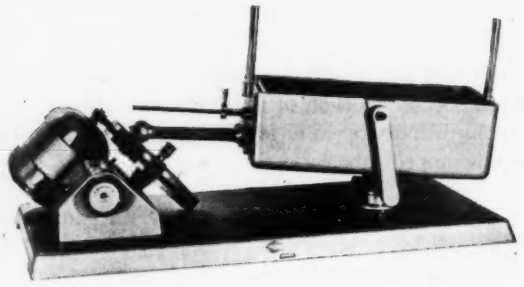

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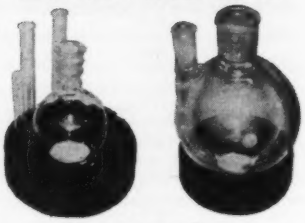

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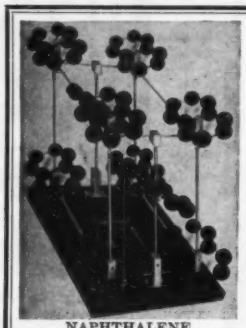

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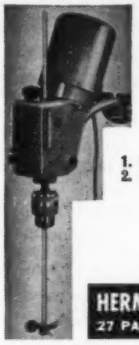

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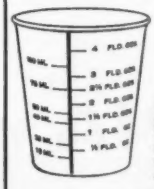

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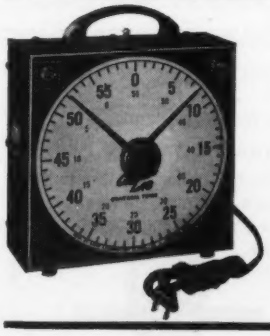

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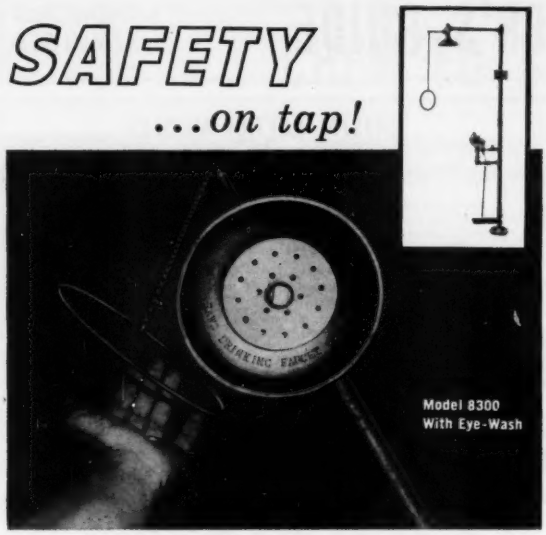

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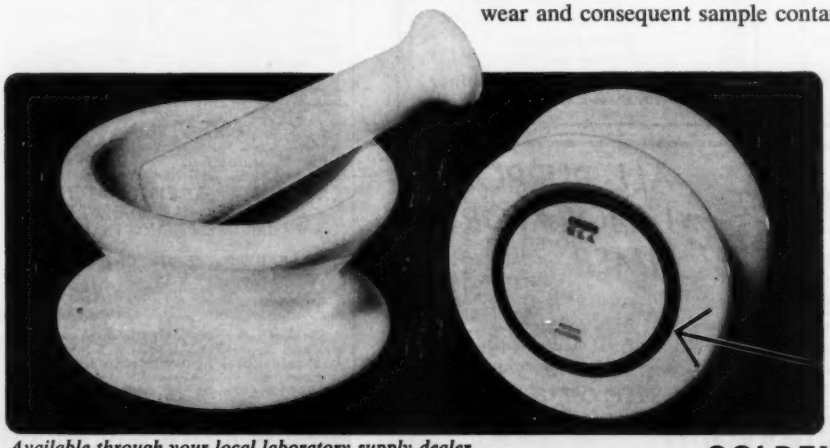

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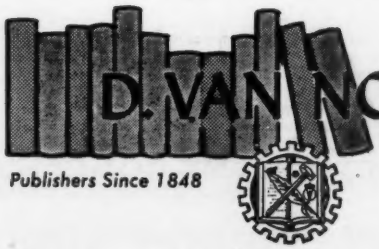

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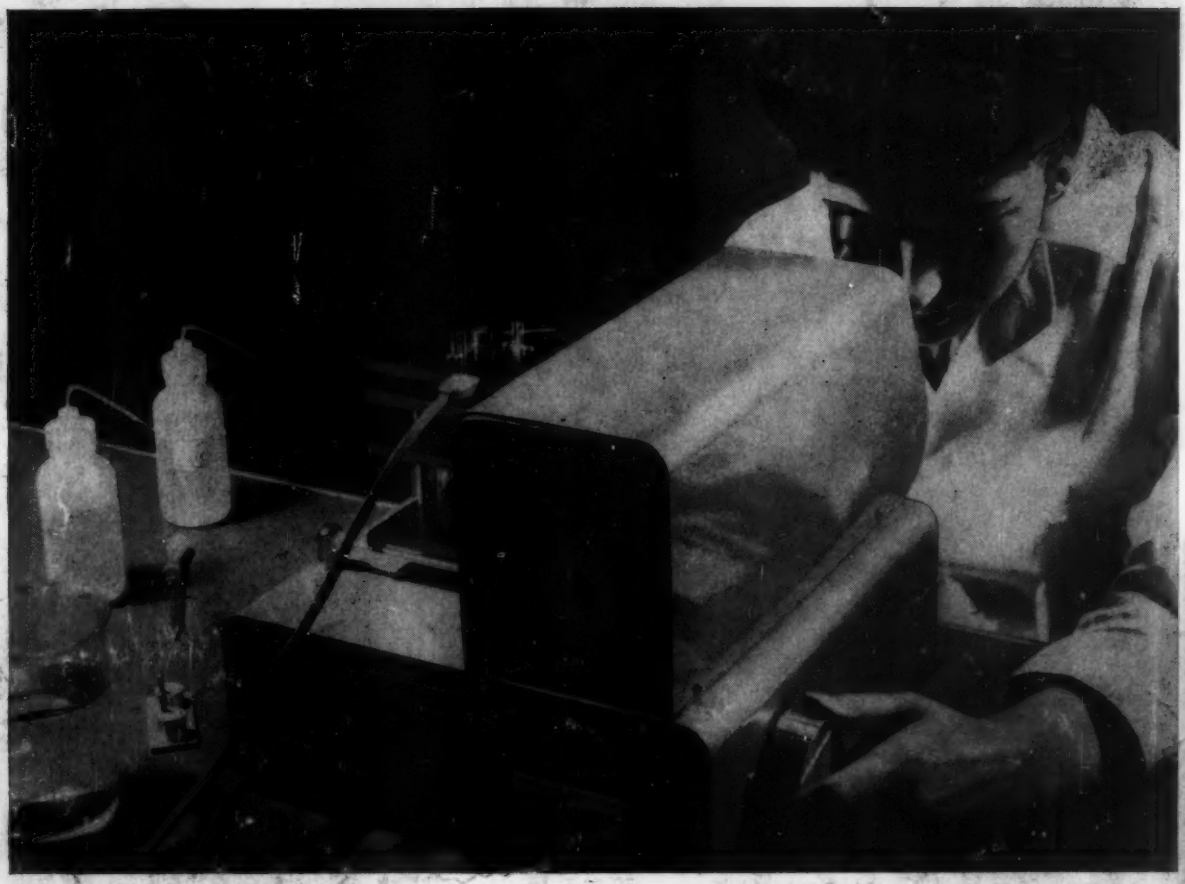

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